

Superatom Thermoelectric Materials

2cd Multifunctional Materials for Defense Workshop

30 July 2012



Materials & Manufacturing Directorate

AFRL/RXBT

Dr. Douglas Dudis

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 30 JUL 2012		2. REPORT TYPE		3. DATES COVERED 00-00-2012 to 00-00-2012	
4. TITLE AND SUBTITLE Superatom Thermoelectric Materials			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory, AFRL/RXBT, Materials & Manufacturing Directorate, Wright Patterson AFB, OH, 45433			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES Presented at the 2nd Multifunctional Materials for Defense Workshop in conjunction with the 2012 Annual Grantees'/Contractors' Meeting for AFOSR Program on Mechanics of Multifunctional Materials & Microsystems Held 30 July - 3 August 2012 in Arlington, VA. Sponsored by AFRL, AFOSR, ARO, NRL, ONR, and ARL.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 50	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			



Team Members / Collaborators



Government

Dr. Douglas Dudis

Dr. John Ferguson

Ms. Angela Campo

Mr. Joel Schmidt

Non-Government

Mr. Michael Check

Mr. Peter Borton

Dr. Chenggang Chen

Mr. Evan Kemp

Mr. Joel Shumaker (UDRI) – Organic Chemistry

Dr. Nicholas Gothard

Dr. Bevan Elliott

Prof. Tahir Cagin (Texas A&M University)

Prof. Michael Leamy (Georgia Tech)



Outline



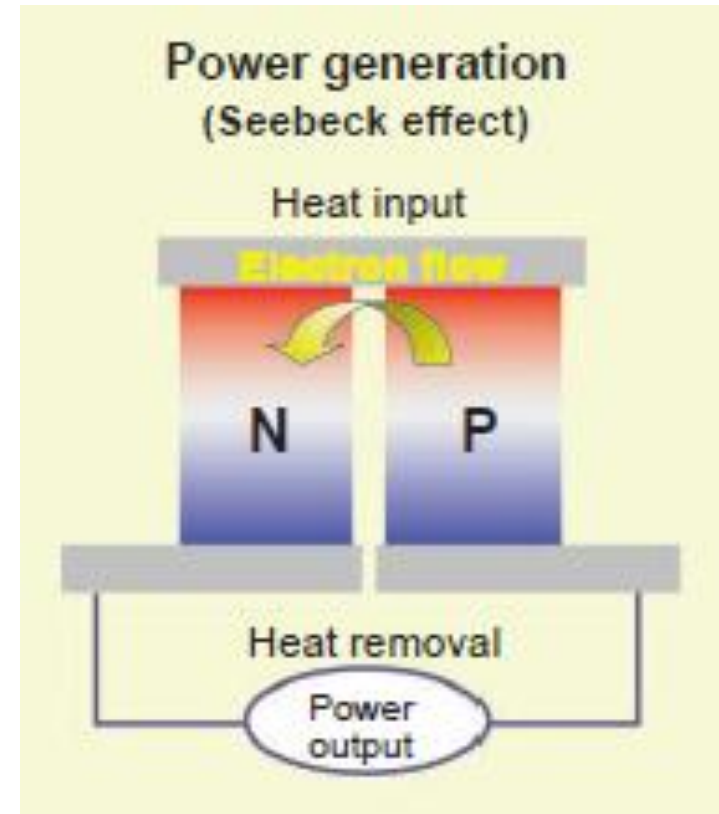
- **Thermoelectrics**
- **Materials Challenges**
- **Advantages of Superatoms**
- **Fullerenes/Fullerides**
- **Progress**
- **Conclusions**



Thermoelectric Architecture



- Two materials in contact
 - N and P refer to desired direction that the electron wants to travel through the material
 - Examine electrons for P-type and holes for N-type
- Temperature differential allows for electron to be excited and released

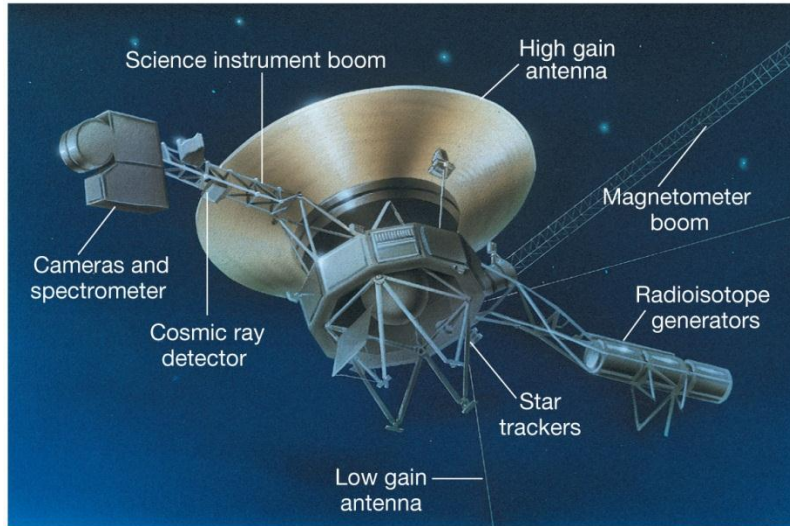


ANALOGIES:

Mechanical: Solid State Heat Pump
Photovoltaic: electrons are working fluid
Energy Harvester with thermal excitation instead of light



Where TE's are used today...



© 2011 Pearson Education, Inc.
<http://www.aerospaceweb.org>
voyager spacecraft



**AMERIGON'S
GENERATOR**
positions semiconductors
between the exhaust stream
and a cooled outer surface
to produce electricity.

Amerigon.com



Newsroom.orange.co.uk/



Thermoelectric Interest & Relevance



AF Impacts Advantages

DEW Lasers

Precision Temp Control

Satellites

Reconfigurable, Long Life, No Vibrations

Pilot Suits

Independent of Orientation & g-forces

UAVs, Sensors

Efficient for small applications

Electronics

Solid State, switchable



**Refrigeration & Heating
Heat Lift & Rejection
Energy Harvesting**

Air Force Research Laboratory TE Interest

Propulsion Directorate (AFRL/RZ)

Human Effectiveness (AFRL/RZH)

Directed Energy Directorate (AFRL/RD)

Air Vehicle Directorate (AFRL/RB)

Space Vehicles Directorate (AFRL/RV)

Information Directorate (AFRL/RI)

Materials & Manufacturing Directorate (AFRL/RX)



Thermoelectric Efficiencies

**If you want to cool a meat locker, use vapor compression cycle.
If you want to cool a hot dog, use a thermoelectric.**

Specific Power:

High Eff. Stirling 25 kW est.:	220 W/kg
NASA Stirling 5 kW System:	140 W/kg
Bi-Te Thermoelectric 14.7 W:	300 W/kg

Similarly, thermoelectric energy harvesting on small scale can be better than other options.

***UAV ~ 100W generator based on waste heat reutilization.
Replace mechanically based generator.
(ongoing program)***

Notion that thermoelectrics are inefficient is misguided – question of scale.



Scramjet Characteristics

Power and Thermal Challenges



- **X-51 Waverider:**
Longest duration
scramjet flight 2+
minutes at Mach 5
- **High Speed Strike**
Weapon

Thermal

- High temperature heat loads
 - Large surface area
 - ΔT - array of fuel cooling paths
- Heat capacity of fuel as heat sink
- Air inlet drag limitations
- Altitude - convection

Power

- No rotating shaft
- High electrical power requirements
- Inlet air drag
- Altitude – air breathing technologies

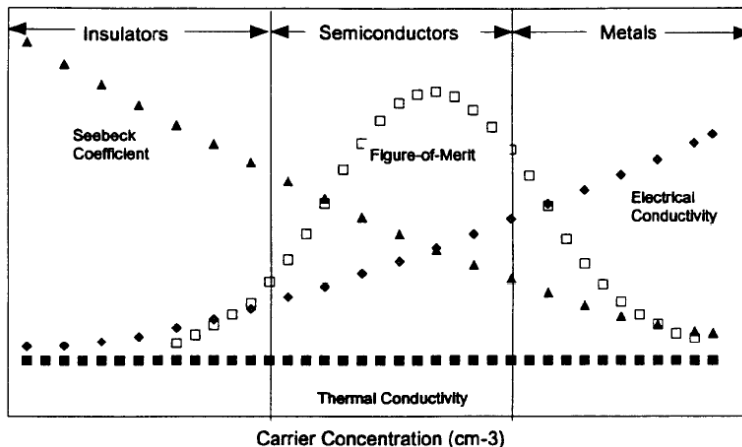


Relation to Thermoelectric Materials



$$ZT = \frac{(S(T))^2 \cdot \sigma(T)}{\kappa_e(T) + \kappa_l(T)} \cdot T$$

We want a phonon glass,
electron crystal material.



Periodic Table of the Elements

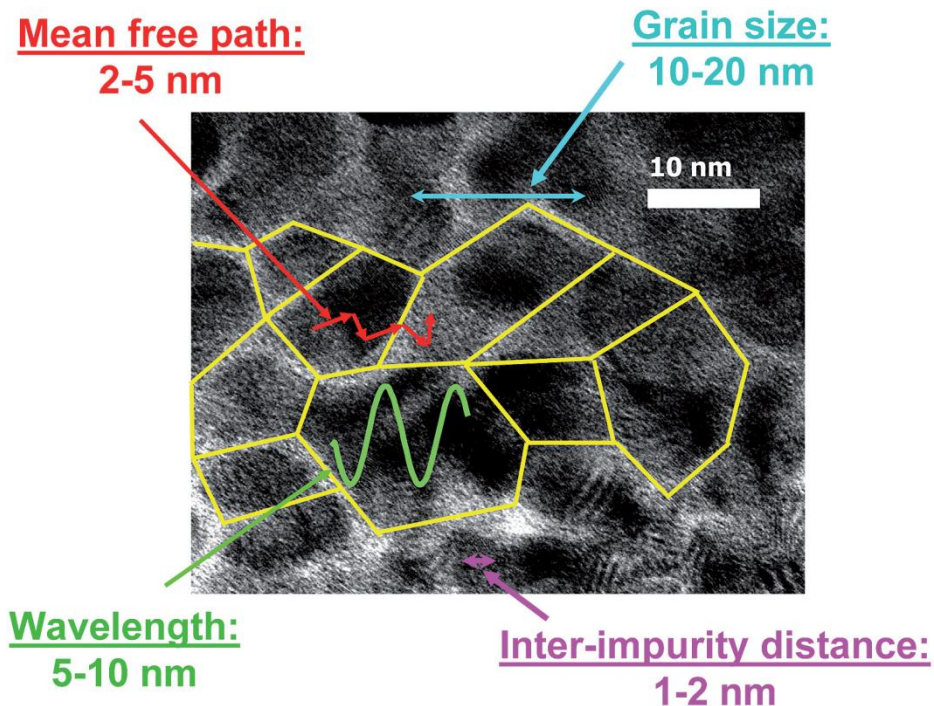
1A	1	H	2	He	O
1A	3	Li	4	Be	1A
1A	11	Na	12	Mg	1A
1A	19	K	20	Ca	1A
1A	37	Rb	38	Sr	1A
1A	55	Cs	56	Ba	1A
1A	87	Fr	88	Ra	1A
1A	101	La	102	Ce	1A
1A	103	Pr	104	Nd	1A
1A	105	Pm	106	Sm	1A
1A	107	Eu	108	Gd	1A
1A	109	Tb	110	Dy	1A
1A	111	Ho	112	Er	1A
1A	113	Tm	114	Yb	1A
1A	115	Lu	116		1A
1A	117		118		1A
1A	119		120		1A
1A	121		122		1A
1A	123		124		1A
1A	125		126		1A
1A	127		128		1A
1A	129		130		1A
1A	131		132		1A
1A	133		134		1A
1A	135		136		1A
1A	137		138		1A
1A	139		140		1A
1A	141		142		1A
1A	143		144		1A
1A	145		146		1A
1A	147		148		1A
1A	149		150		1A
1A	151		152		1A
1A	153		154		1A
1A	155		156		1A
1A	157		158		1A
1A	159		160		1A
1A	161		162		1A
1A	163		164		1A
1A	165		166		1A
1A	167		168		1A
1A	169		170		1A
1A	171		172		1A
1A	173		174		1A
1A	175		176		1A
1A	177		178		1A
1A	179		180		1A
1A	181		182		1A
1A	183		184		1A
1A	185		186		1A
1A	187		188		1A
1A	189		190		1A
1A	191		192		1A
1A	193		194		1A
1A	195		196		1A
1A	197		198		1A
1A	199		200		1A
1A	201		202		1A
1A	203		204		1A
1A	205		206		1A
1A	207		208		1A
1A	209		210		1A
1A	211		212		1A
1A	213		214		1A
1A	215		216		1A
1A	217		218		1A
1A	219		220		1A
1A	221		222		1A
1A	223		224		1A
1A	225		226		1A
1A	227		228		1A
1A	229		230		1A
1A	231		232		1A
1A	233		234		1A
1A	235		236		1A
1A	237		238		1A
1A	239		240		1A
1A	241		242		1A
1A	243		244		1A
1A	245		246		1A
1A	247		248		1A
1A	249		250		1A
1A	251		252		1A
1A	253		254		1A
1A	255		256		1A
1A	257		258		1A
1A	259		260		1A
1A	261		262		1A
1A	263		264		1A
1A	265		266		1A
1A	267		268		1A
1A	269		270		1A
1A	271		272		1A
1A	273		274		1A
1A	275		276		1A
1A	277		278		1A
1A	279		280		1A
1A	281		282		1A
1A	283		284		1A
1A	285		286		1A
1A	287		288		1A
1A	289		290		1A
1A	291		292		1A
1A	293		294		1A
1A	295		296		1A
1A	297		298		1A
1A	299		300		1A
1A	301		302		1A
1A	303		304		1A
1A	305		306		1A
1A	307		308		1A
1A	309		310		1A
1A	311		312		1A
1A	313		314		1A
1A	315		316		1A
1A	317		318		1A
1A	319		320		1A
1A	321		322		1A
1A	323		324		1A
1A	325		326		1A
1A	327		328		1A
1A	329		330		1A
1A	331		332		1A
1A	333		334		1A
1A	335		336		1A
1A	337		338		1A
1A	339		340		1A
1A	341		342		1A
1A	343		344		1A
1A	345		346		1A
1A	347		348		1A
1A	349		350		1A
1A	351		352		1A
1A	353		354		1A
1A	355		356		1A
1A	357		358		1A
1A	359		360		1A
1A	361		362		1A
1A	363		364		1A
1A	365		366		1A
1A	367		368		1A
1A	369		370		1A
1A	371		372		1A
1A	373		374		1A
1A	375		376		1A
1A	377		378		1A
1A	379		380		1A
1A	381		382		1A
1A	383		384		1A
1A	385		386		1A
1A	387		388		1A
1A	389		390		1A
1A	391		392		1A
1A	393		394		1A
1A	395		396		1A
1A	397		398		1A
1A	399		400		1A
1A	401		402		1A
1A	403		404		1A
1A	405		406		1A
1A	407		408		1A
1A	409		410		1A
1A	411		412		1A
1A	413		414		1A
1A	415		416		1A
1A	417		418		1A
1A	419		420		1A
1A	421		422		1A
1A	423		424		1A
1A	425		426		1A
1A	427		428		1A
1A	429		430		1A
1A	431		432		1A
1A	433		434		1A
1A	435		436		1A
1A	437		438		1A
1A	439		440		1A
1A	441		442		1A
1A	443		444		1A
1A	445		446		1A
1A	447		448		1A
1A	449		450		1A
1A	451		452		1A
1A	453		454		1A
1A	455		456		1A
1A	457		458		1A
1A	459		460		1A
1A	461		462		1A
1A	463		464		1A
1A	465		466		1A
1A	467		468		1A
1A	469		470		1A
1A	471		472		1A
1A	473		474		1A
1A	475		476		1A
1A	477		478		1A
1A	479		480		1A
1A	481		482		1A
1A	483		484		1A
1A	485		486		1A
1A	487		488		1A
1A	489		490		1A
1A	491		492		1A
1A	493		494		1A
1A	495		496		1A
1A	497		498		1A
1A	499		500		1A
1A	501		502		1A
1A	503		504		1A
1A	505		506		1A
1A	507		508		1A
1A	509		510		1A
1A	511		512		1A
1A	513		514		1A
1A	515		516		1A
1A	517		518		1A
1A	519		520		1A
1A	521		522		1A
1A	523		524		1A
1A	525		526		1A
1A	527		528		1A
1A	529		530		1A
1A	531		532		1A
1A	533		534		1A
1A	535		536		1A
1A	537		538		1A
1A	539		540		1A
1A	541		542		1A
1A	543		544		1A
1A	545		546		1A
1A	547		548		1A
1A	549		550		1A
1A	551		552		1A
1A	553		554		1A
1A	555		556		1A
1A	557		558		1A
1A	559		560		1A
1A	561		562		1A
1A	563		564		1A
1A	565		566		1A
1A	567		568		1A
1A	569		570		1A
1A	571		572		1A
1A	573		574		1A
1A	575		576		1A
1A	577		578		1A
1A	579		580		1A
1A	581		582		1A
1A	583		584		1A
1A	585		586		1A
1A	587		588		1A
1A	589		590		1A
1A	591		592		1A
1A	593		594		1A
1A	595		596		1A
1A	597		598		1A
1A	599		600		1A
1A	601		602		1A
1A	603		604		1A
1A	605		606		1A
1A	607		608		1A
1A	609		610		1A
1A	611		612		1A
1A	613		614		1A
1A	615		616		1A
1A	617		618		1A
1A	619		620		1A
1A	621		622		1A
1A	623		624		1A
1A	625		626		1A
1A	627		628		1A
1A	629		630		1A
1A	631		632		1A
1A	633		634		1A
1A	635		636		1A
1A	637		638		1A
1A	639		640		1A
1A	641		642		1A
1A	643		644		1A
1A	645		646		1A
1A	647		648		1A
1A	649		650		1A
1A	651		652		1A
1A	653		654		1A
1A	655		656		1A
1A	657		658		1A
1A	659		660		1A
1A	661		662		1A
1A	663		664		1A
1A	665		666		1A
1A	667		668		1A
1A	669		670		1A
1A	671		672		1A
1A	673		674		

$\sigma(T)$ is electrical conductivity [S/cm]
 $\kappa(T)$ is thermal conductivity [W/(m*K)]
 $S(T)$ is the Seebeck coefficient/thermopower [$\mu\text{V/K}$]

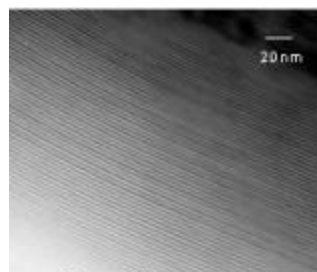


Current Approaches

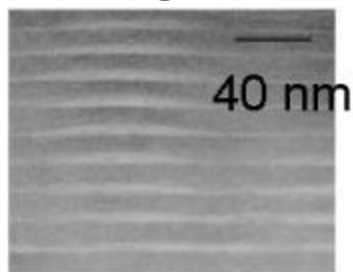
- **Decreasing thermal conductivity contribution**
 - Nanostructuring
 - Superlattices (2D), nanowires (1D), and quantum dots (0D)
 - Doping with heavier element
 - Allows for lower sound velocities
 - i.e. $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$, $\text{Si}_{80}\text{Ge}_{20}$



- **Electron Filtering**



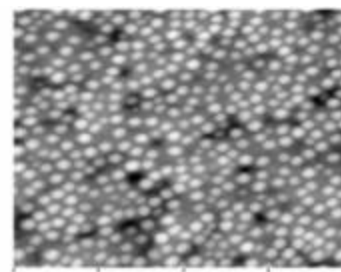
Bulk



Superlattice



Nanowire



Quantum Dots

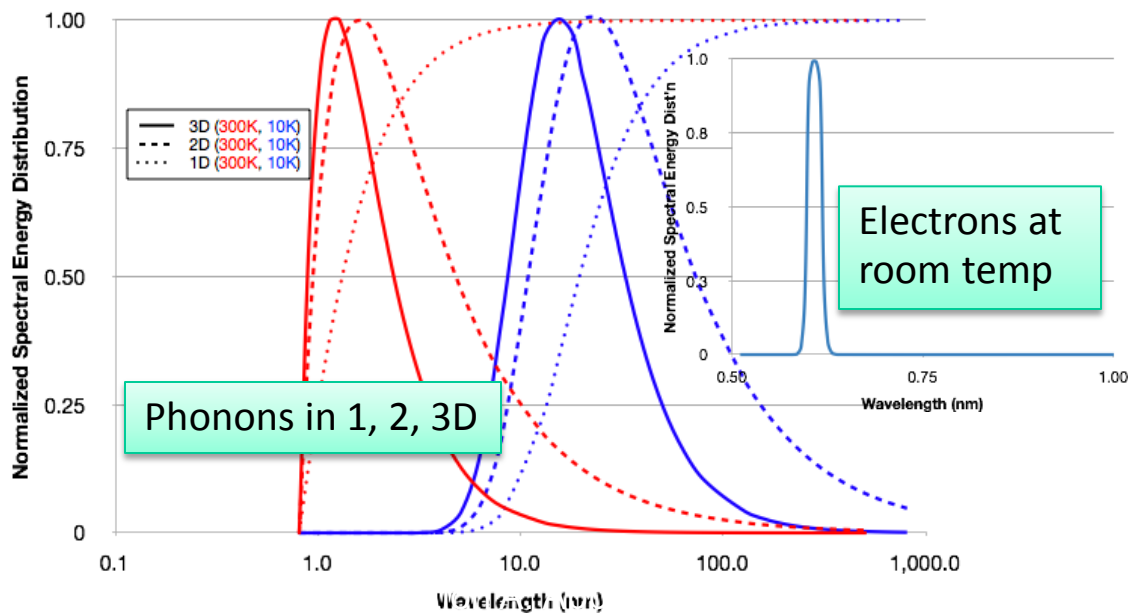


Phonon Glass Electron Crystals

PGEC: G. A. Slack, in “CRC Handbook of Thermoelectrics,” edited by D. M Rowe (CRC Press, London), 1995, p. 407.

An ideal thermoelectric material will behave like a crystal in terms of electrical conductivity, but will behave like a glass in terms of thermal conductivity.

Electron wavelengths and phonon wavelengths are very different : can be decoupled.

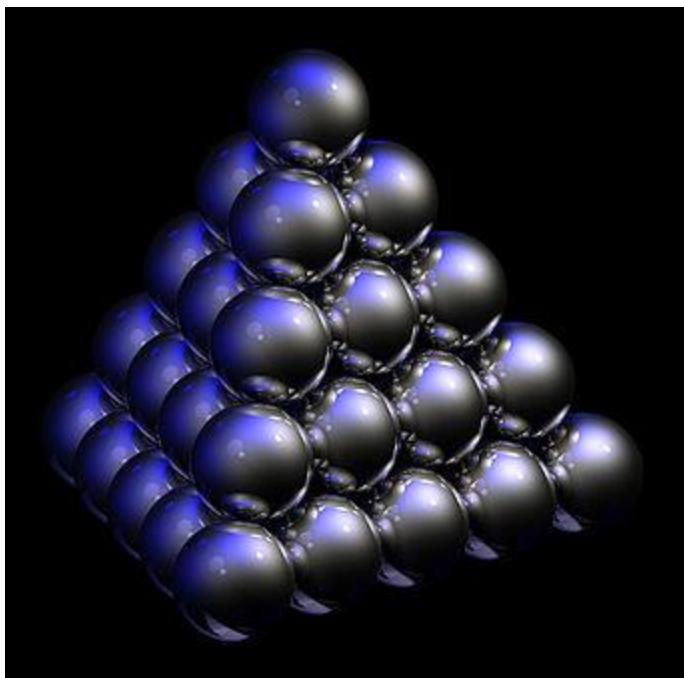


High σ / High κ Graphite Silver	High σ / Low κ ???
Low σ / High κ Diamond	Low σ / Low κ Polymers Molecular Matls

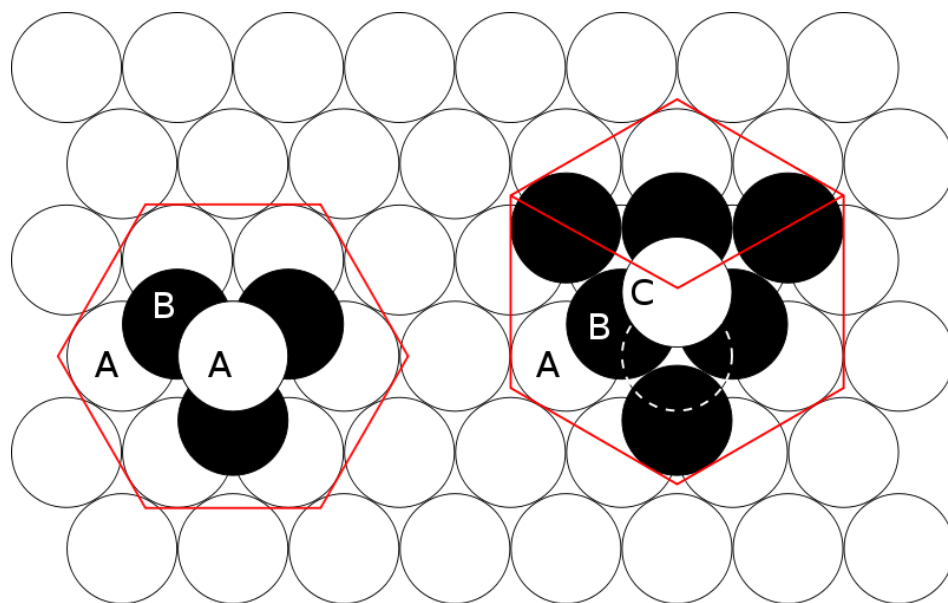
Fullerides as PGECs



Closest Packing Considerations: AgI Fast Ion Conduction



<http://en.wikipedia.org/wiki/Close-packing>



Silver Iodide: Great Example of Size Mismatch in CP Structures

Room Temperature: Wurtzite Structure

Ag^+ 1.15 Å (115 pm)

Above 147 °C, NaCl Structure

I^- 2.20 Å (220 pm)

Becomes Fast Ion Conductor (the silver sub-lattice melts)



Diminished Thermal Conductivity in Nanowires

Importance of Interfaces

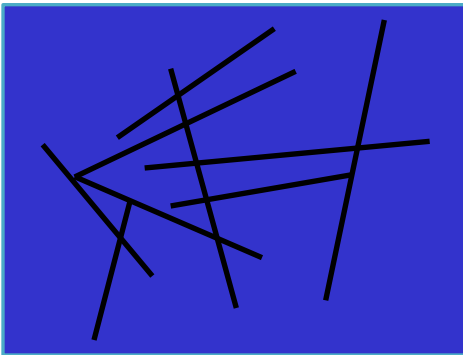


Silicon Nanowires as Efficient Thermoelectric Materials

A. I. Bouka, Y. Bunimovich, J. Tahir-Kheli, J.-K. Yu, W. A. Goddard, J. R. Heath, **Nature Letters**, **451**, 2008, 168-171.

Enhanced Thermoelectric Performance of Rough Silicon Nanowires

A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett, M. Najarian, A. Majumdar, and P. Yang, **Nature Letters**, **451**, 2008, 163-168.



- Diameter of nanowire $<$ phonon mean free path
- Charge can hop (real particle); phonon can't

“While nanostructured thermoelectric materials can increase $ZT > 1$, the materials (Bi, Te, Pb, Sb and Ag) and processes used are not often easy to scale to practically useful dimensions.”



Build Thermoelectric Materials Incorporating Superatoms



Superatoms ~ cluster than can behave as a unit / have characteristics similar to an atom.

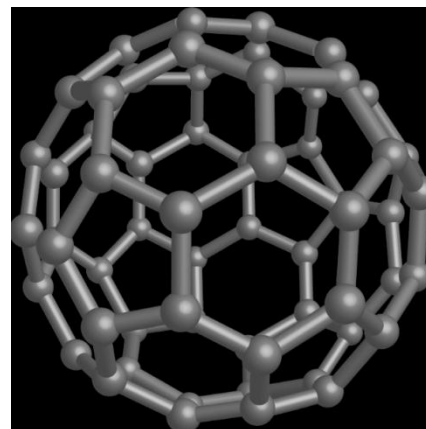
**Diamond
CNTs (Parallel)**

~ 2000+ W/mK



CNTs (vdW)

~ 10 W/mK



Buckyball

~ 0.5 W/mK

While fullerenes can be thought of as closest packing like atomic closest packing, there is a size mismatch relative to thermal energy transport. Within a buckyball, coupling length ~ 0.14 nm, but from inter-buckyball length ~ 1.5 nm.



C_{60} Characteristics

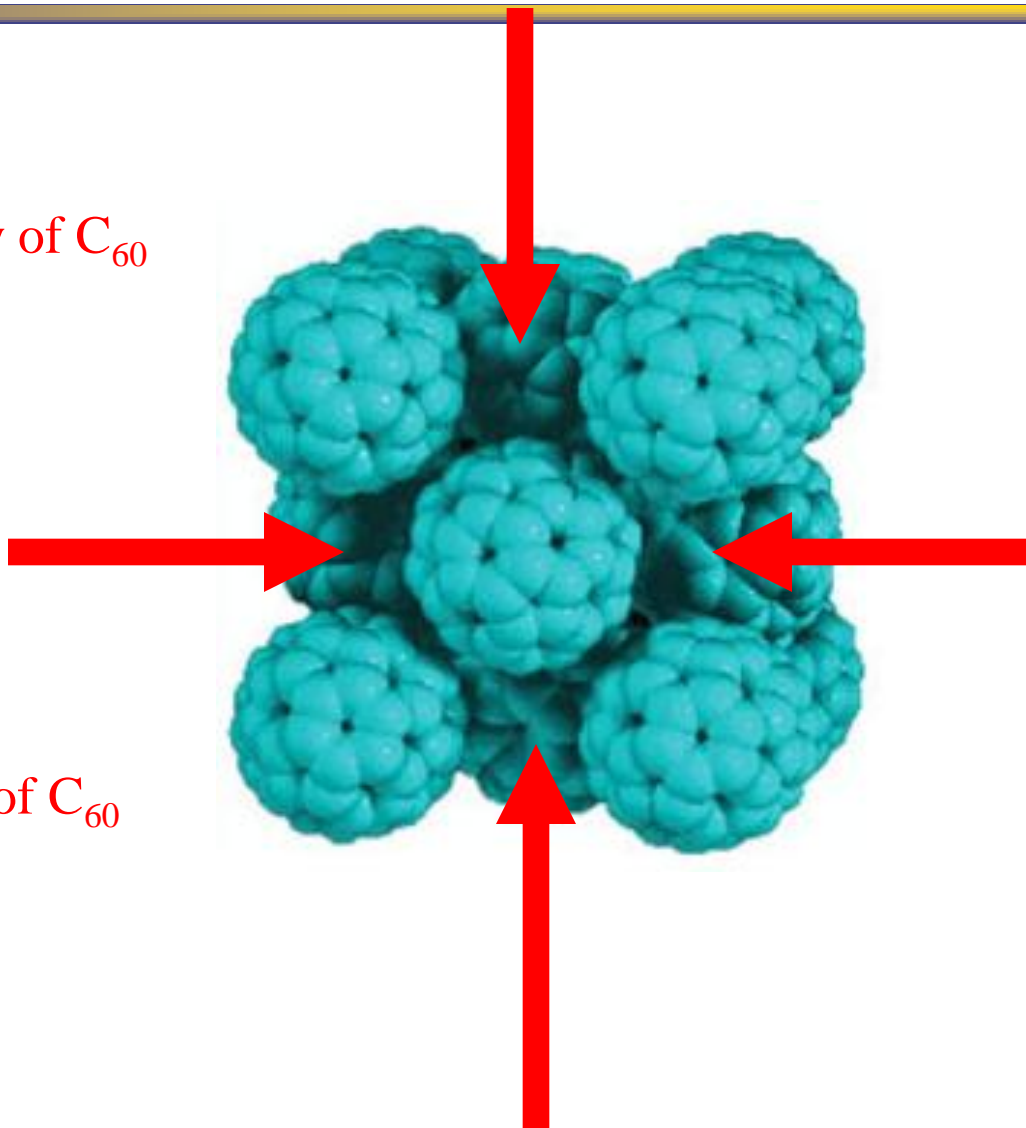


Goal: Increase electrical conductivity of C_{60}

How? **Fulleride formation**

Goal: Decrease thermal conductivity of C_{60}

How? **Fulleride formation**

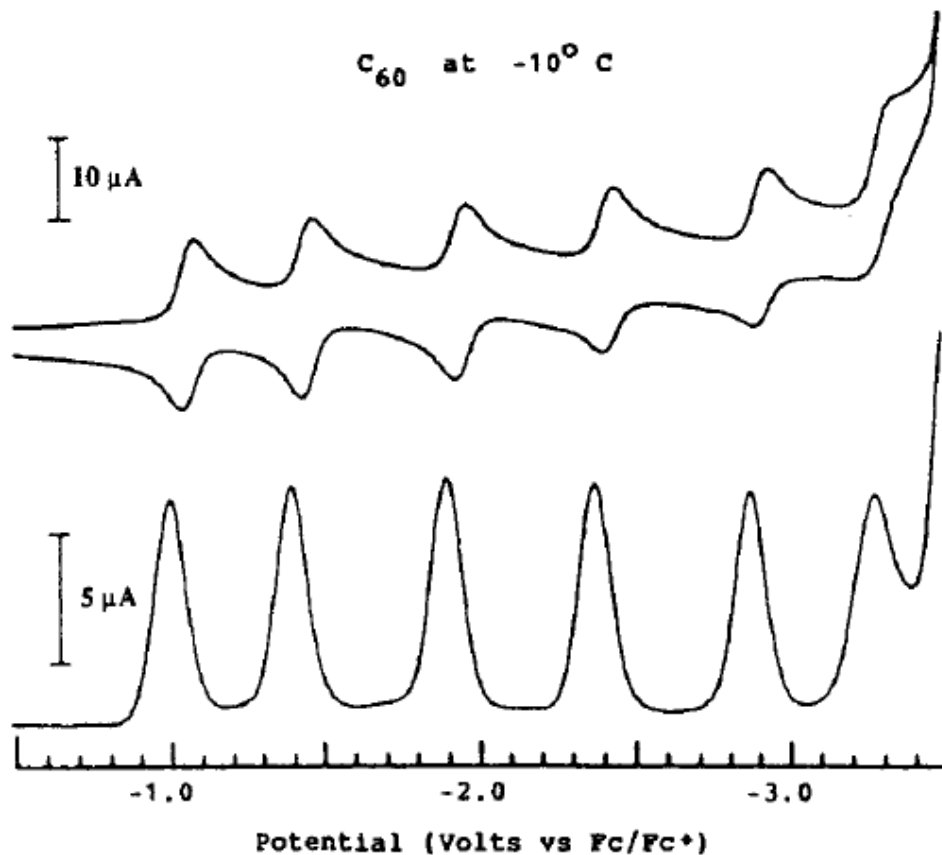
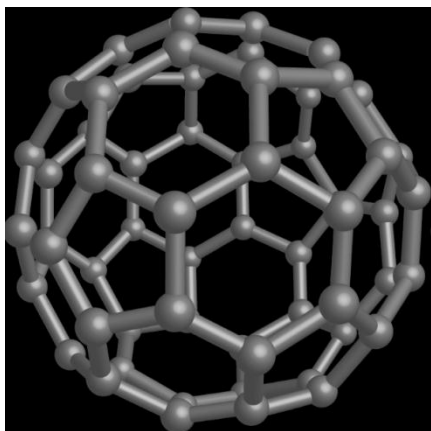


Fullerides as PGECs



Why C_{60} ?

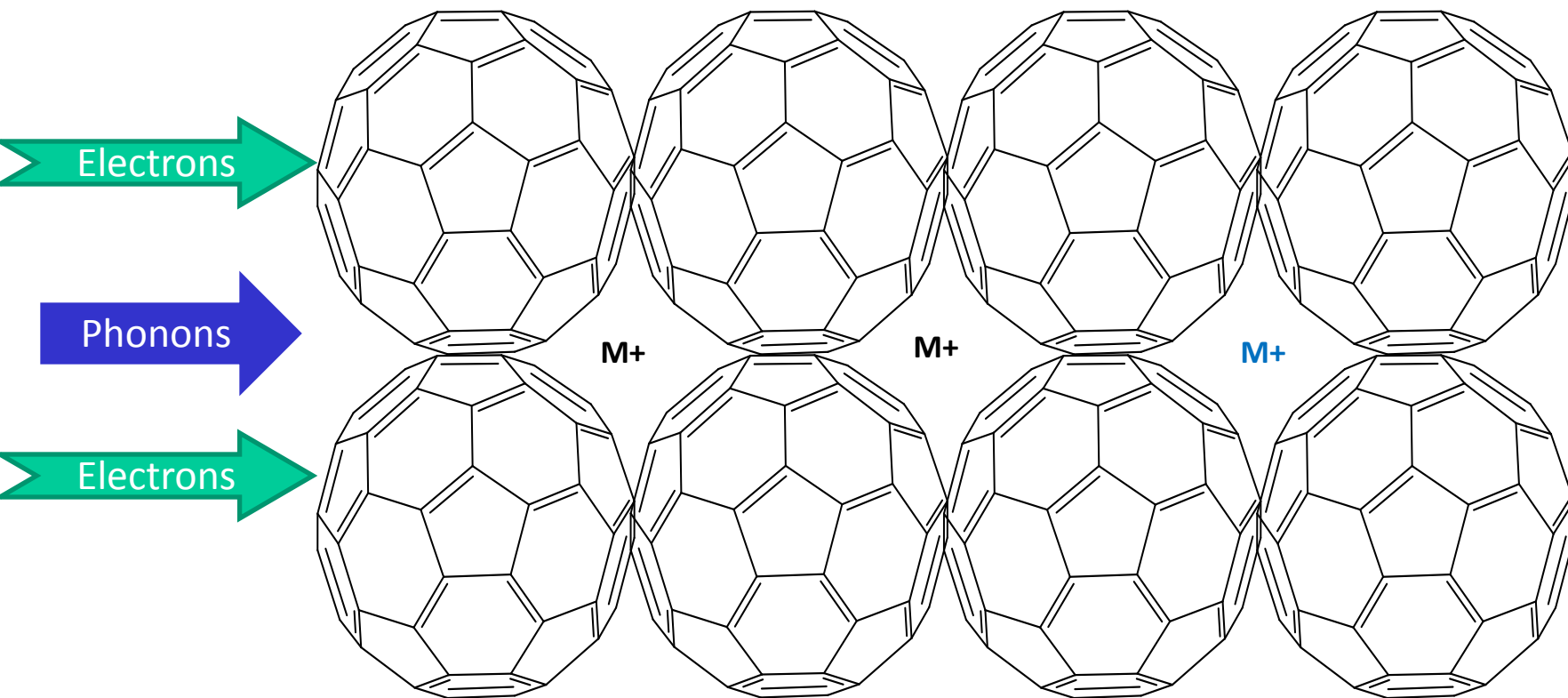
- Inherently low thermal conductivity
- Similar to skutterudites
- Multiple charge/spin states



Potential for Jahn-Teller Distortion:
 "Selective e-phonon coupling" ?



Rattler Effect in Fullerides



- **Gigantic Rattler Effect?**
- **Alloying Enhancements (Lowering) of κ**
- **Uncouples electron and & phonon transport**

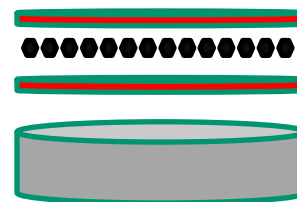


Synthesis of Materials



•Thin Film

- Performed in a deep vacuum deposition chamber
- Used magnetron sputtering to deposit zinc and thermal evaporator to deposit C_{60}

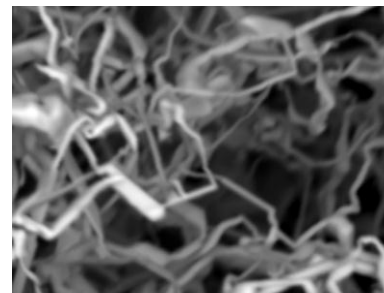


•Wet Synthesis

- Based on redox potentials of transition metals

•Chemical Vapor Deposition

- Grown in a process using a zoned furnace system and vacuum system



2012/01/24 13:50 H D4.6 x10k 10 um



2012/01/24 13:50 H D4.6 x10k 10 um



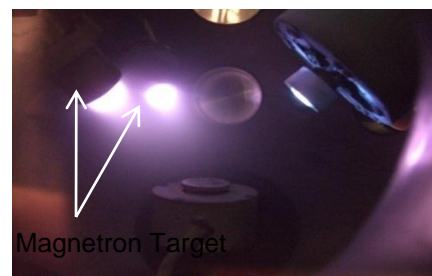
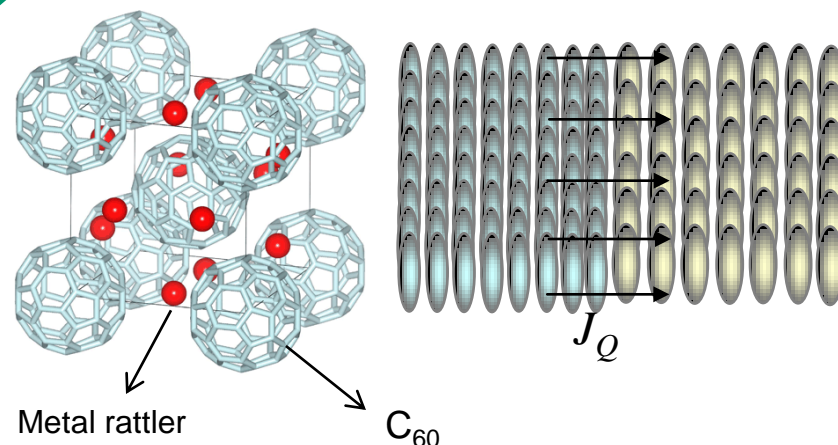
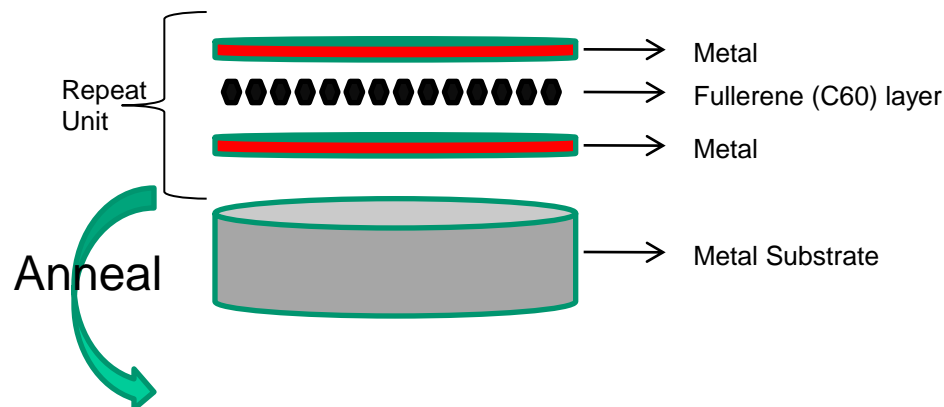
High Electrical Conductivity Phonon Blocking Layers



Objective: Demonstration of high electrical conductivity, low thermal conductivity phonon-blocking layer (PBL) formation through novel deposition and annealing techniques

Novel concepts addressed :

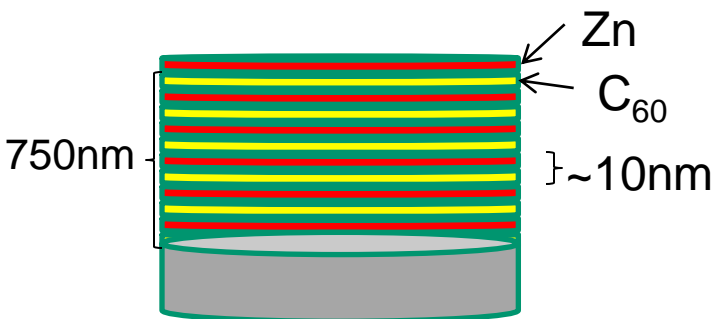
- Incorporation of nanoparticle scattering sites inside a thin film structure
- Demonstration of an air stable metal fulleride (Zn C_{60})
- Demonstration of low thermal conductivity and high electrical conductivity of fulleride (rattlers)
- Demonstrate the use of thin film deposition technique for use in combinatorial analysis.



$$Z = \frac{S(T)^2 \sigma(T)}{\kappa(T)}$$

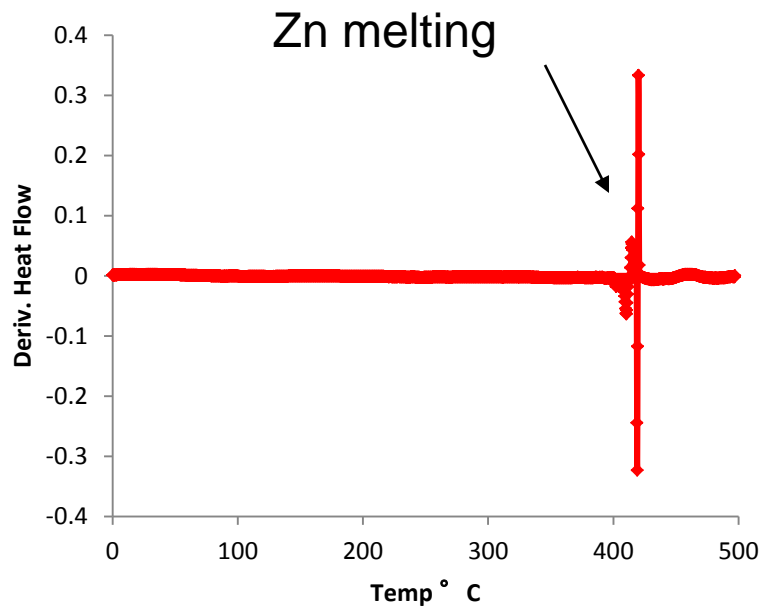


DSC of Zn C₆₀ layers

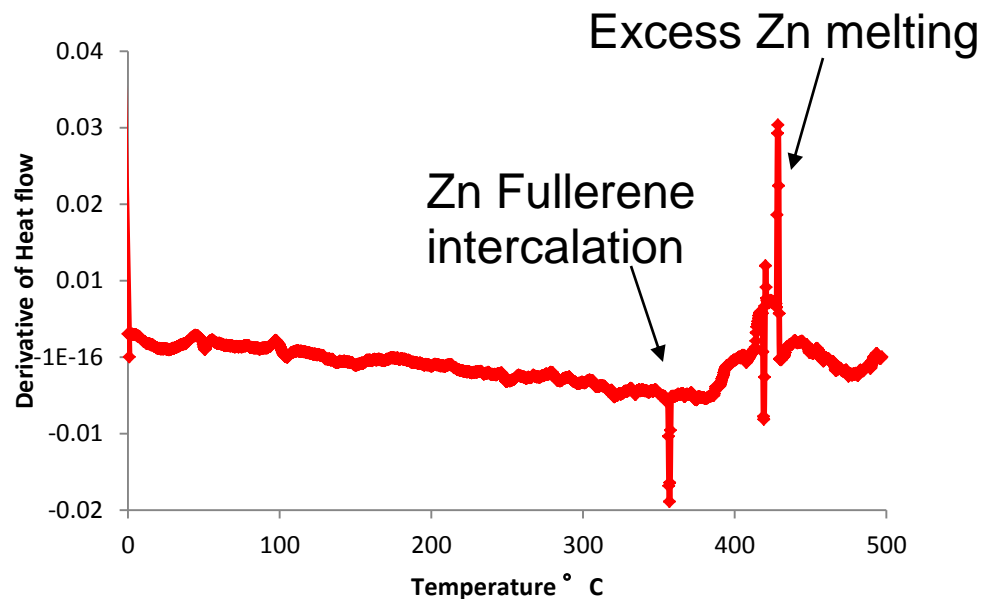


- Sample made with 75 layers. Each layer was ~10nm thick with alternating Zn/C₆₀
- Looking for exotherms and endotherms on DSC to confirm Zn intercalation into the C₆₀

Deriv. Heat Flow Pure Zn

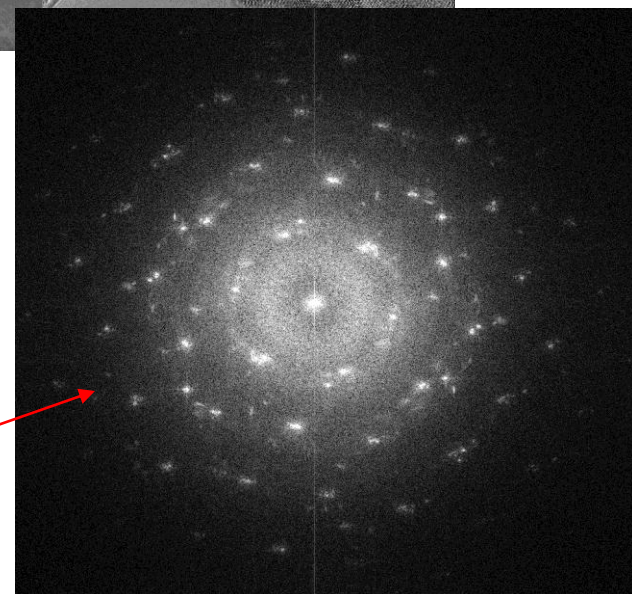
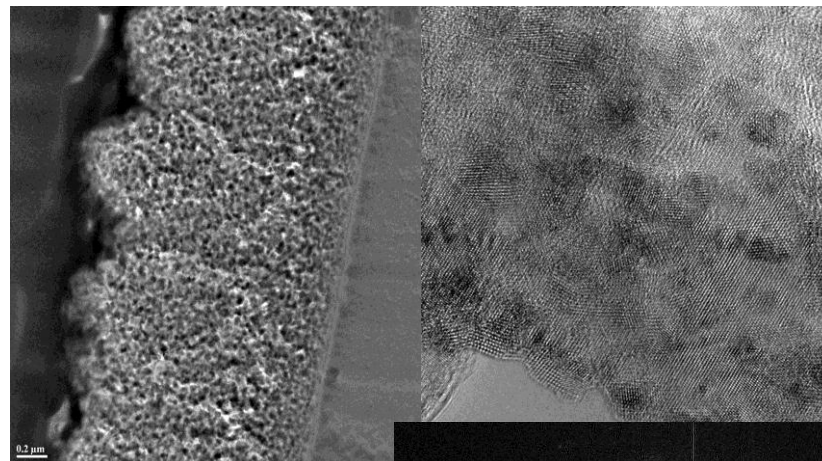
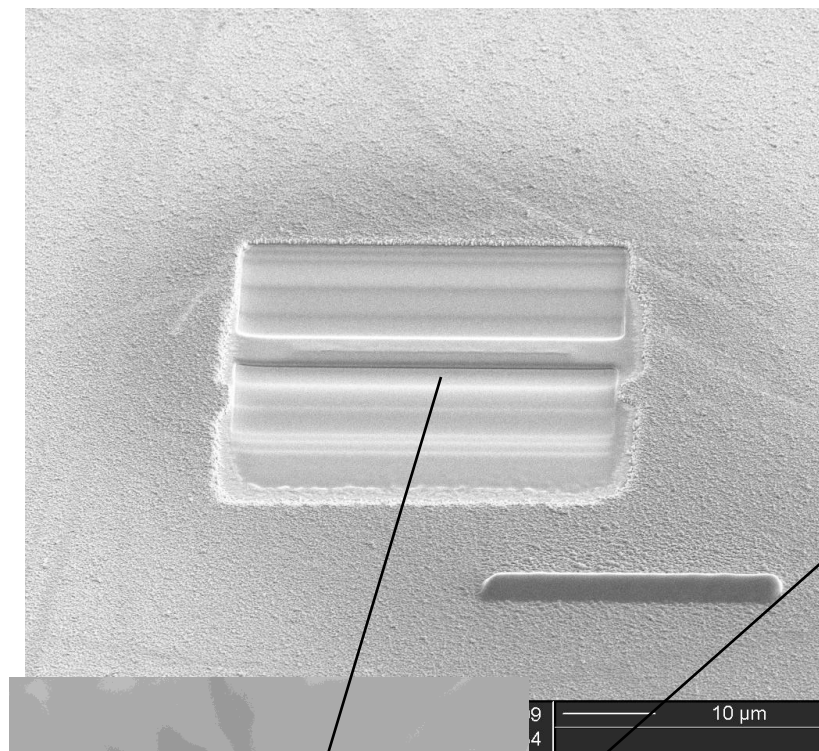


75 Layers Zn-C60 DSC (Derivative of Heat Flow)





TEM and e⁻ Diffraction

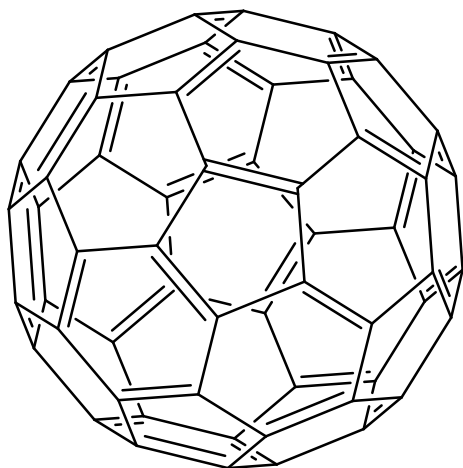


Does not show a
separate phase for
Zn



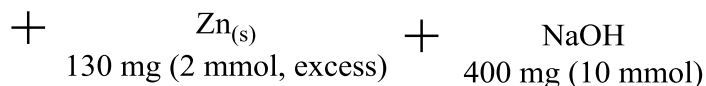


Wet Chemical Approaches



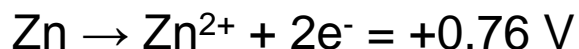
C_{60}
34 mg (0.047 mmol)

Reactants and solvent was mixed together
in glove box to remove all oxygen



20 mL of THF

Reactants do not dissolve in THF, vial is
sealed with a septum and removed from
glove box

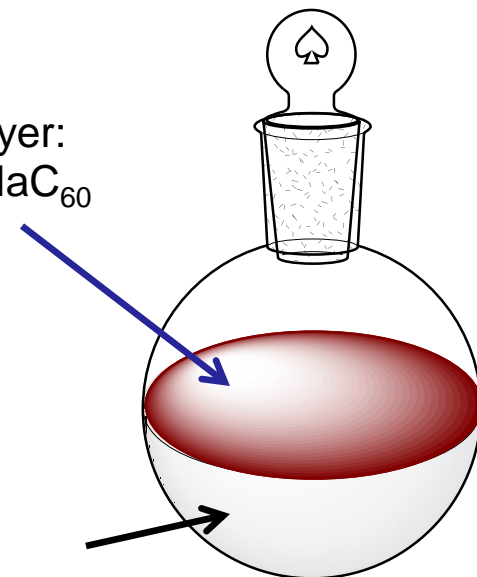


**5 mL of de-oxygenated water is added via
syringe**

- Water was boiled for 20 minutes to removed non-
condensed gases, then cooled and mineral oil was
added to the surface, then nitrogen was bubbled through
water for 30 minutes

Rapid reaction occurred, H_2 gas evolved, two layers produced

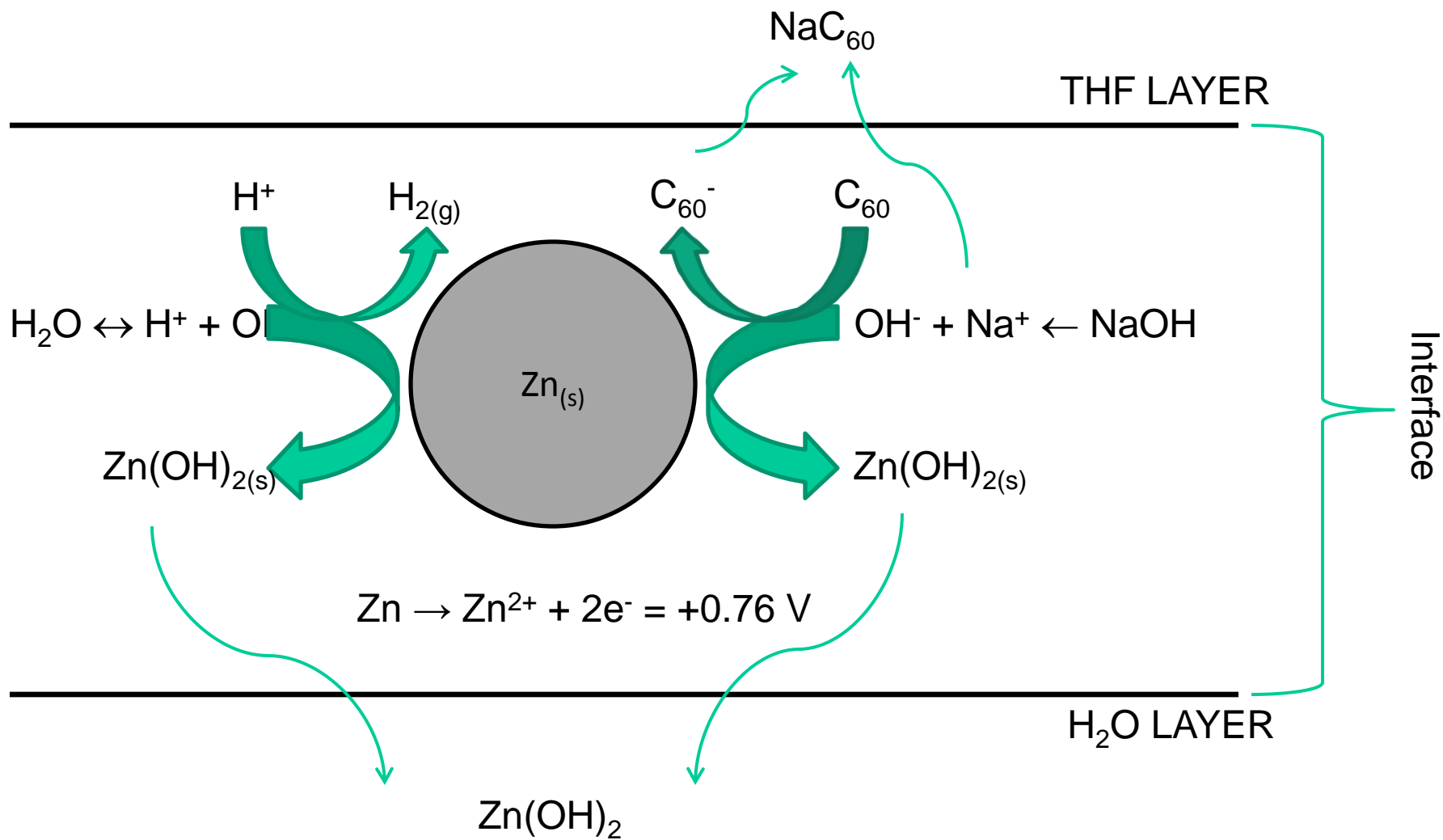
Top Layer:
THF + NaC_{60}



Bottom Layer:
 $H_2O + \text{Zn}(\text{OH})_2$ + unreacted starting material



Proposed Mechanism of Reaction





Synthetic Protocol for Metal Fullerides



Procedure: Based on Redox Potentials of Starting Materials and Solvents and Activity Series of Metals Involved

Reactants and solvent was mixed together
in glove box to remove all oxygen

C_{60}
34 mg (0.047 mmol)

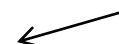
+

$Zn_{(s)}$
130 mg (2 mmol, excess)

+

$Zn(OH)_2$
1 g (10 mmol)

$Zn(NO_3)_2 + NaOH$



20 mL of THF

Reactants do not dissolve in THF, vial is
sealed with a septum and removed from
glove box

5 mL of de-oxygenated water is added via
syringe

- Water was boiled for 20 minutes to removed non-
condensed gases, then cooled and mineral oil was added to
the surface, then nitrogen was bubbled through water for 30
minutes

Reaction occurred much slower, H_2 gas evolved, two layers produced to an extent
Sodium Nitrate Contaminants!

Top Layer = THF + $Zn_x(C_{60})_y$

Bottom Layer = $H_2O + Zn(OH)_2$ + unreacted starting materials



Standard Reduction Potentials for Fullerene



$E_{1/2}$ of various C_{60} anions in solvents in 0.1 M (TBA)ClO₄

Solvent	C_{60}^0/C_{60}^-	C_{60}^-/C_{60}^{2-}	C_{60}^{2-}/C_{60}^{3-}	C_{60}^{3-}/C_{60}^{4-}
THF	-0.33	-0.92	-1.49	-1.99
THF	-0.35	-0.93	-1.43	-2.01
DMF	-0.26	-0.72	-1.31	-1.85
DMSO	-0.16	-0.66	---	---

Reduction Potentials of C_{60}

Solvent	C_{60}^0/C_{60}^-	C_{60}^-/C_{60}^{2-}	C_{60}^{2-}/C_{60}^{3-}	C_{60}^{3-}/C_{60}^{4-}
ACN	---	-0.735	-1.225	-1.685
DMF	-0.312	-0.772	-1.362	-1.902
Aniline	-0.396	-0.693	-1.158	-1.626
Benzonitr.	-0.397	-0.817	-1.297	-1.807
DCM	-0.468	-0.858	-1.308	-1.758
THF	-0.473	-1.063	-1.633	-2.133
Chloroform.	-0.554	-0.908	---	---

Aprotic Polar Solvents

Dichloromethane

Tetrahydrofuran

Ethyl Acetate

Acetone

DMF

Acetonitrile

DMSO

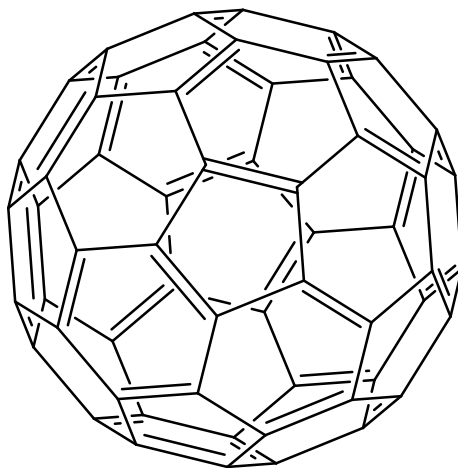
Reaction seems to prefer certain aprotic polar solvents



Standard Reduction Potentials for Viable Metals



Reduction Potential for Metals in Water	
Half-Reaction	E° (V)
$\text{Fe}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Fe}_{(\text{s})}$	-0.44
$\text{Cr}^{3+}_{(\text{aq})} + 3\text{e}^- \rightarrow \text{Cr}_{(\text{s})}$	-0.74
$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Zn}_{(\text{s})}$	-0.76
$\text{Mn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Mn}_{(\text{s})}$	-1.18
$\text{Al}^{3+}_{(\text{aq})} + 3\text{e}^- \rightarrow \text{Al}_{(\text{s})}$	-1.66



C_{60}
0.047 mmol

+

$\text{M}_{(\text{s})}$
2 mmol, excess

+

$\text{M}(\text{OH})_x$
10 mmol



Synthetic Protocol for Metal Fullerides



5.00 g C_{60}
19.1 g $Zn_{(s)}$ granular
1 L THF

Placed into a 2 L round bottom flask,
sealed with a septum, and removed
from the glove box

150 g of freshly made $Zn(OH)_2$
needs to be synthesized

Re-dissolved in 1 L ammonium
hydroxide

$[Zn(NH_3)_4](OH)_2$

Syringed into 2 L round bottom
React at 45 °C for 5 days

Zinc Fulleride (+ 7 grams of product, brown powder)

270.75 g of $Zn(SO_4) \cdot H_2O$ dissolved into 2 L
of water

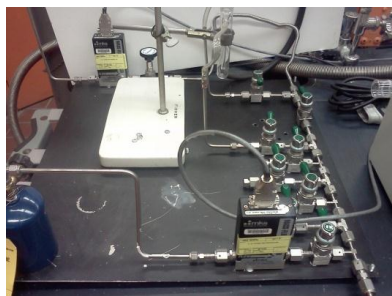
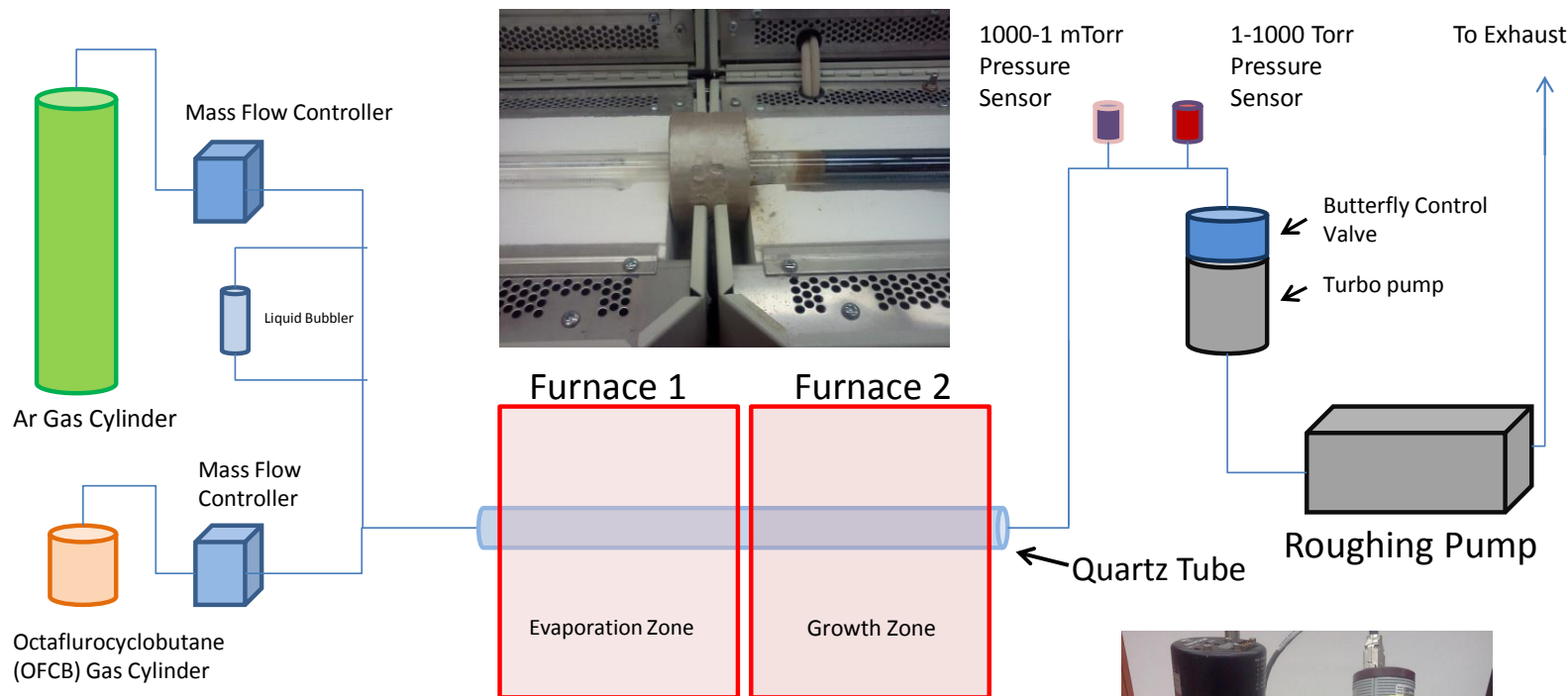
Add 203.75 mL of NH_4OH

$Zn(OH)_2$



Zn Nanowires +

Schematic Layout of CVD system





Zn wires with C60 coating

Hold Zn boat at 950° C/325° C for 15 hr

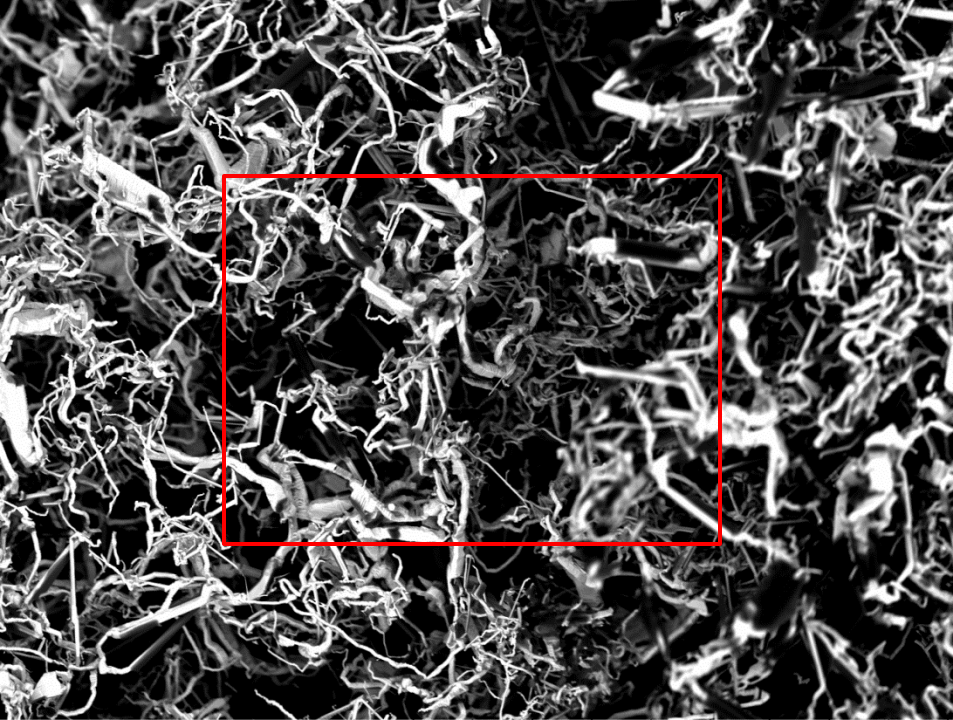
Maintain constant 3 Torr and 50 SCCM Ar

Cool to RT and swap out empty boat for C60 boat

Hold at 1000° C/350° C for 15 hr

Maintain constant 3 Torr and 100 SCCM Ar

Note: All pictures can be enlarged while keeping good picture quality.

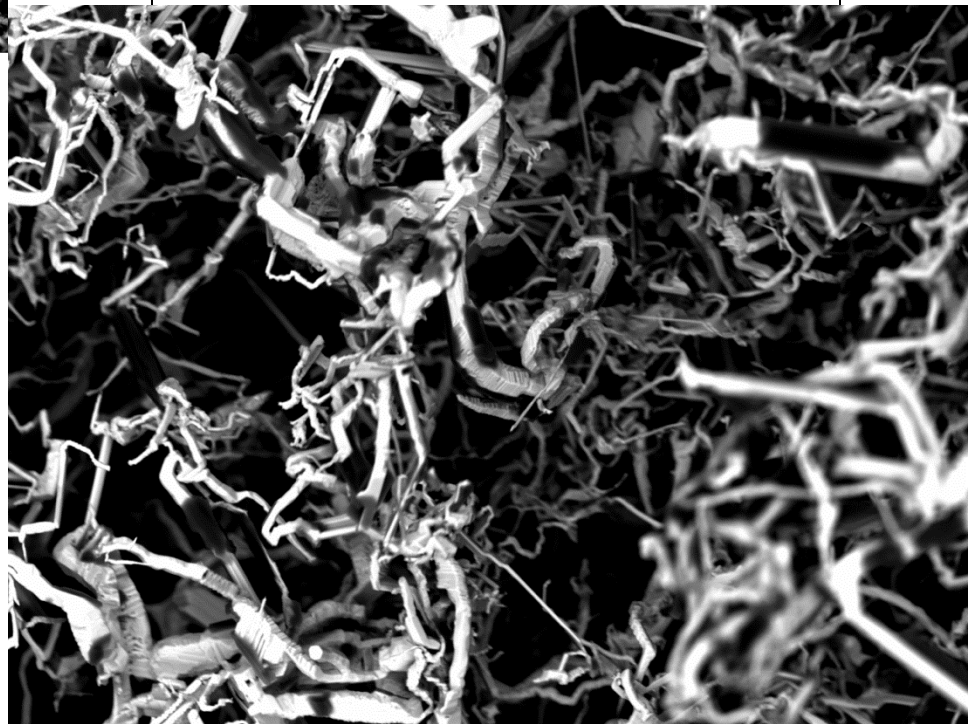


2012/02/03 09:18 H D4.8 x500 200 um



Region 1 (x500)

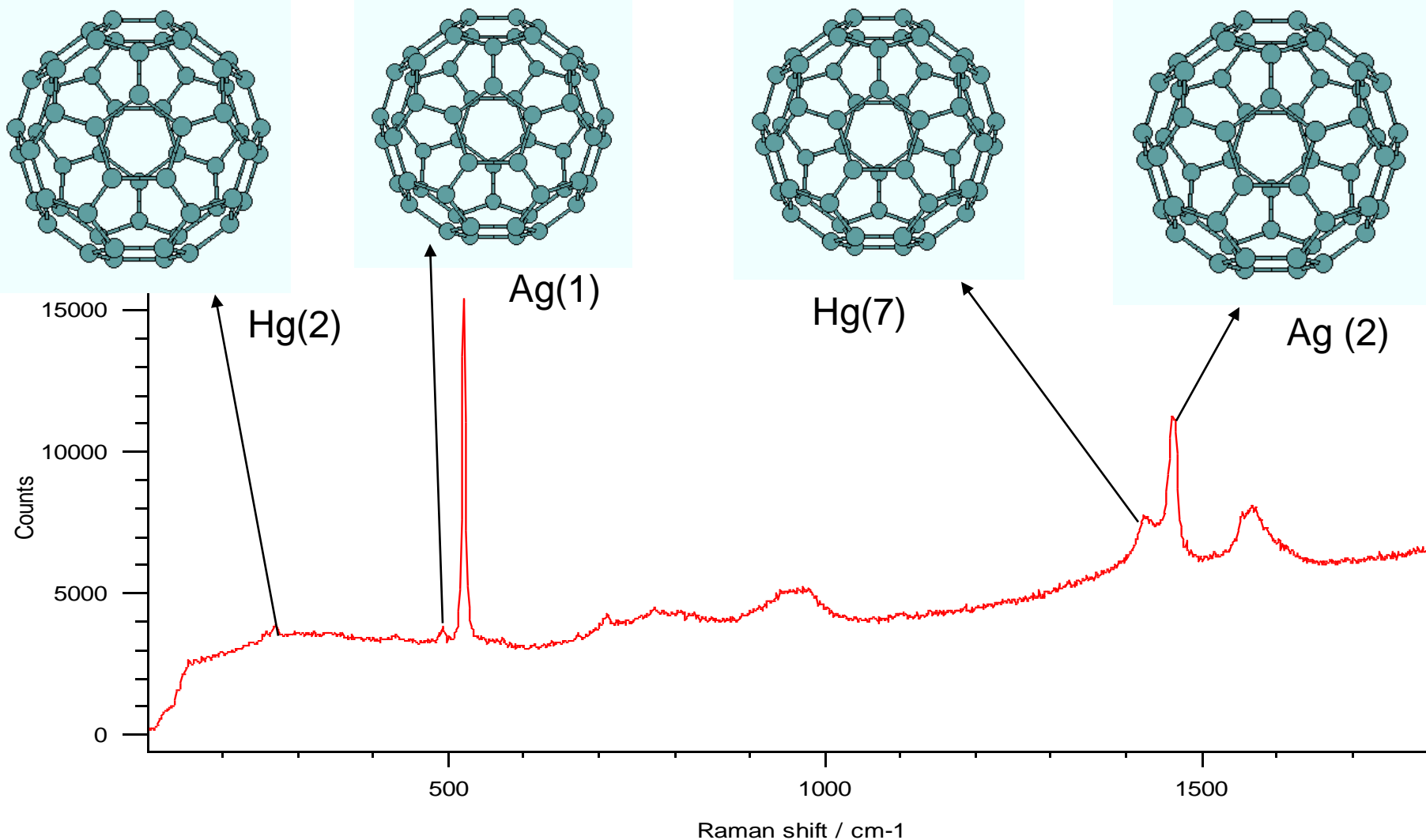
Region 1 (x1000)



2012/02/03 09:20 H D4.8 x1.0k 100 um



Raman Modes in Neutral C₆₀





Raman Spectroscopy of Zn_xC_{60}



Landau damping and lifting of vibrational degeneracy in metallic potassium fulleride

J. Winter and H. Kuzmany

Universität Wien, Institut für Festkörperphysik, Strudlhofgasse 4, A-1090 Wien, Austria

(Received 21 July 1995)

- A rather strong shift of vibrational modes as a consequence of charge transfer
- The electron-phonon interaction may well be considered in case as the reason for the broadening and for the shift of the lines and electron-phonon coupling constants may be deduced
- For the description of the relation between phonon linewidth and electron-phonon coupling constants for a single particle excitation Allen's formula may be used

$$\gamma_i = \frac{1}{g_i} \frac{\pi}{2} N(0) \lambda_i \omega_{bi}^2$$

γ_i Is the full width at half max of the line

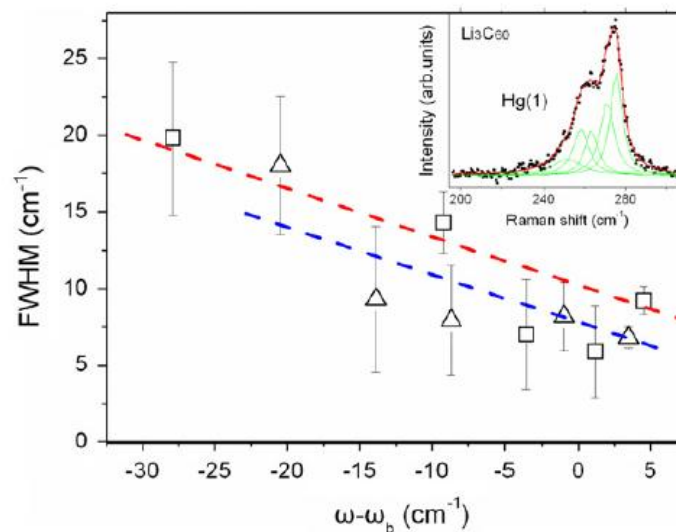
$N(0)$ Density of States at the Fermi level per spin and molecule

λ_i and g_i Dimensionless electron phonon coupling constants

ω_{bi} Bare phonon frequency before coupling to the electrons

Raman study of the electron–phonon interaction in light alkali metal intercalated metallic fullerenes

Mingguang Yao^{1,2}, Vittoria Pischedda¹ and Alfonso San Miguel¹

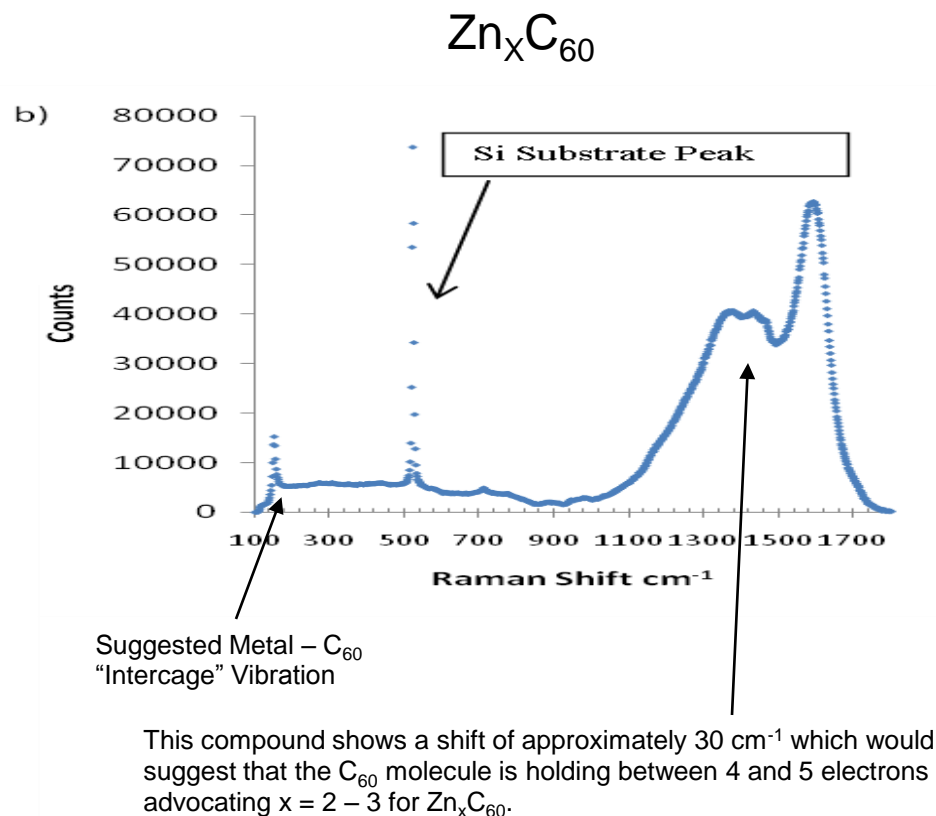
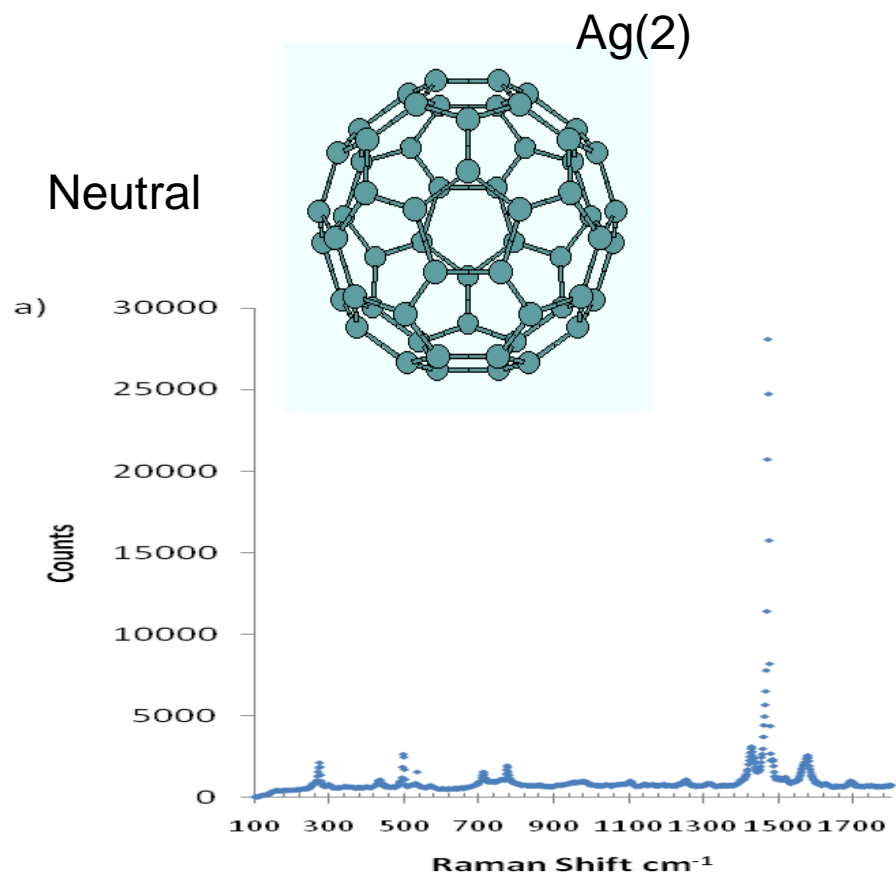


Electron-phonon coupling uses the phonon widths measured in Raman scattering. In metallic systems a phonon can decay in an electron-hole pair excitation. The extra width due to this decay is a measure of the coupling.



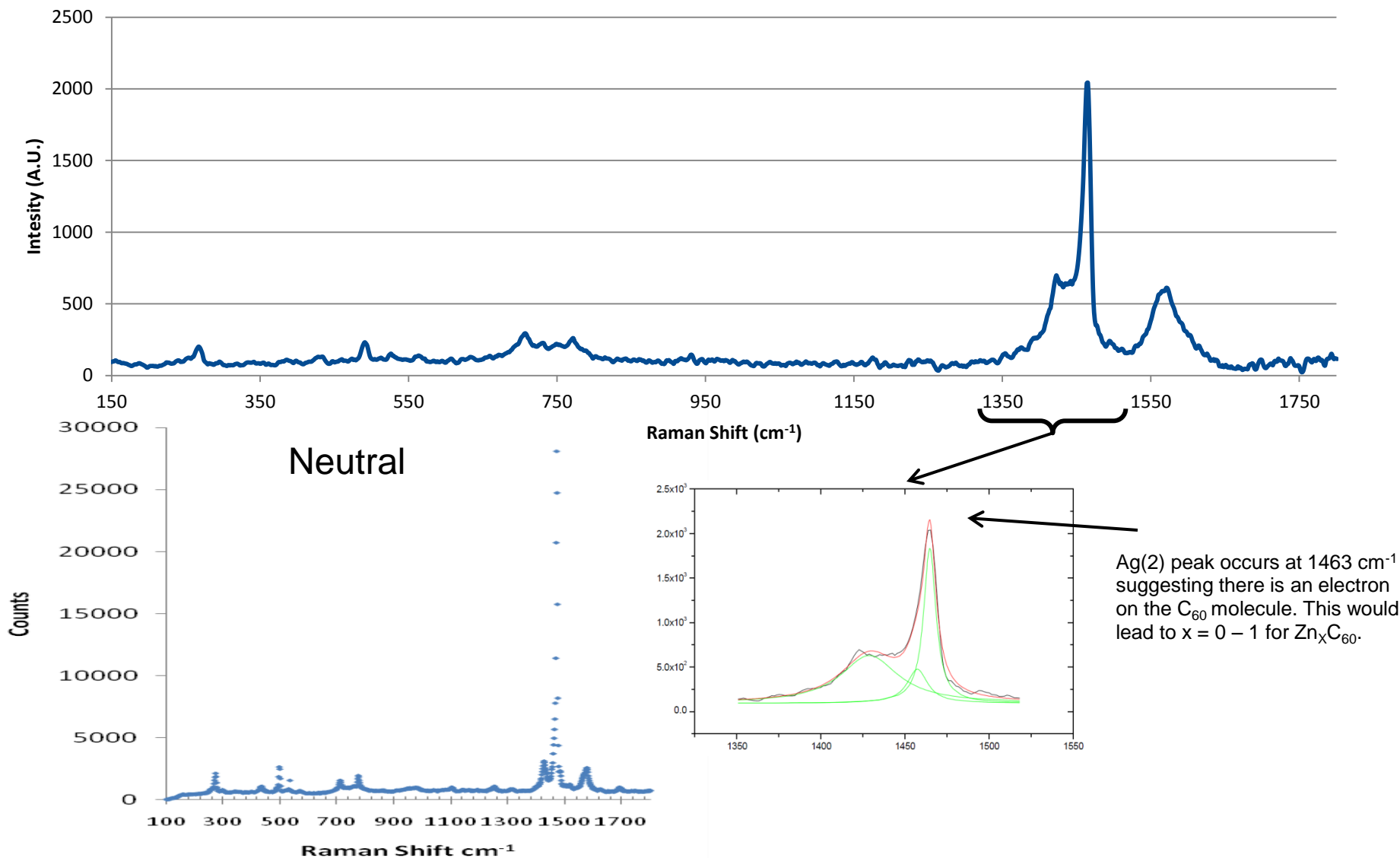
Raman Spectroscopy of Zn_xC_{60} thin film

Sample is 75 Layers of C_{60} and Zn (C_{60} and Zn Layers are 10nm thick) After Annealing in furnace at 400°C



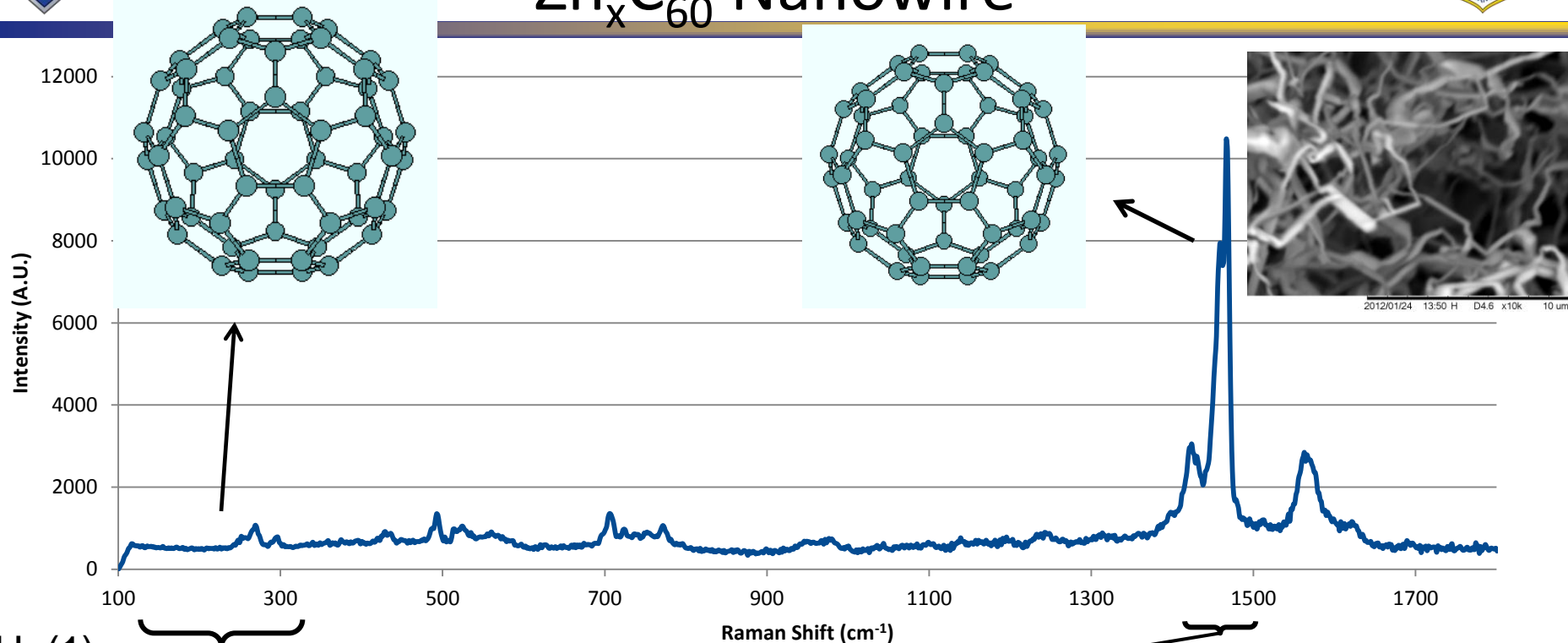


Raman Spectroscopy of Zn_xC_{60} produced by bulk synthesis route

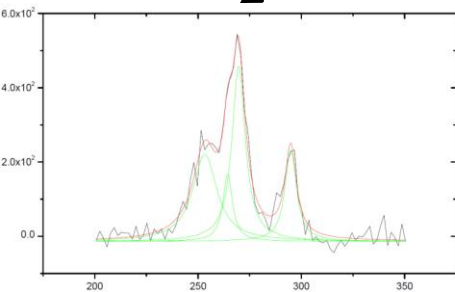




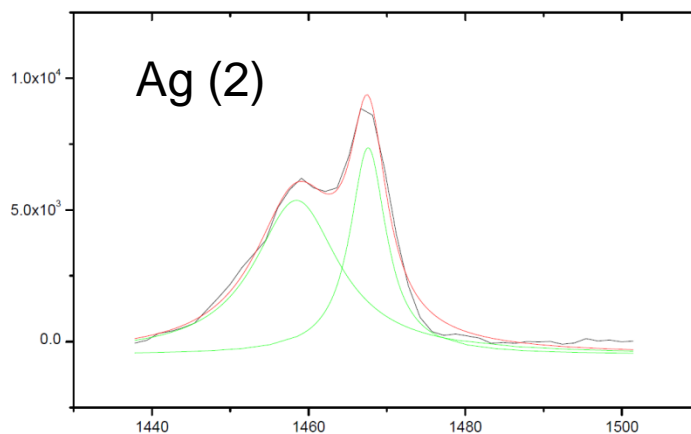
Raman Spectroscopy of Zn_xC_{60} Nanowire



Hg(1)



Ag (2)

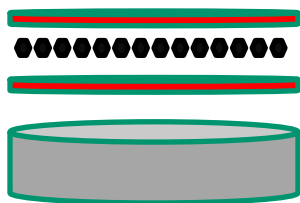


Ag(2) peak occurs at 1468 cm^{-1} and 1458 cm^{-1} which is suggestive of two C₆₀ phases. Approximately 60% of the C₆₀ is incorporated to the nanowire and charged. However, the remainder is most likely in a second phase and not closely associated with the majority zinc wire structure.



Thermal Properties of Fulleride Compound

- Thin Film



$$\kappa = 0.13 \text{ W}/(\text{m}^*\text{K})$$

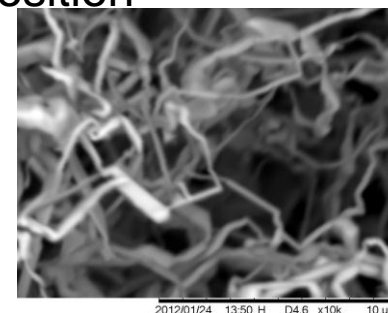
TDTR

- Wet Synthesis

$$\kappa = 0.24 \text{ W}/(\text{m}^*\text{K})$$

HotDisk

- Chemical Vapor Deposition



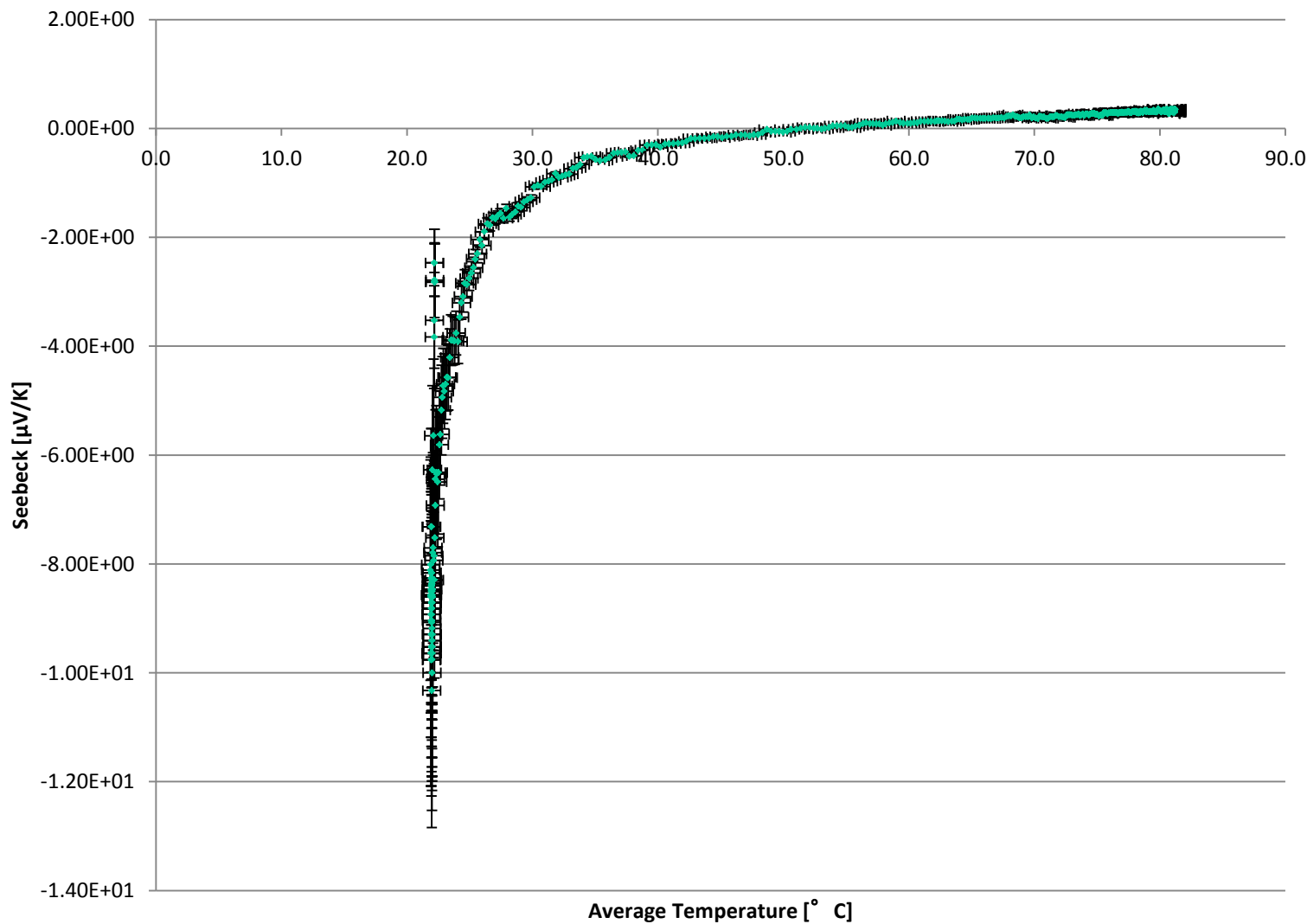
$$\kappa = 3 - 5 \text{ W}/(\text{m}^*\text{K})$$

HotDisk

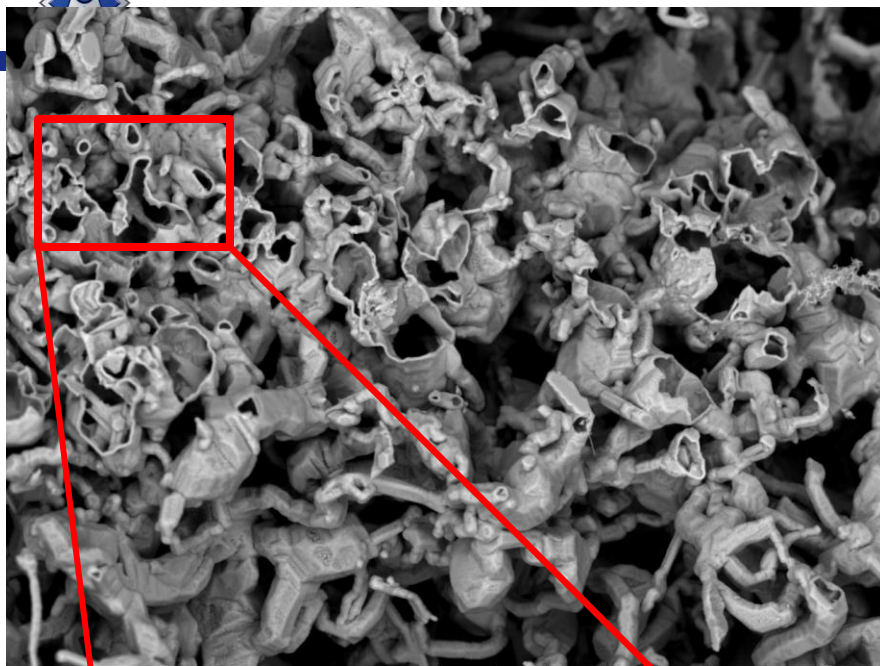
Thermal Conductivity of Glass = $1 \text{ W}/(\text{m}^*\text{K})$



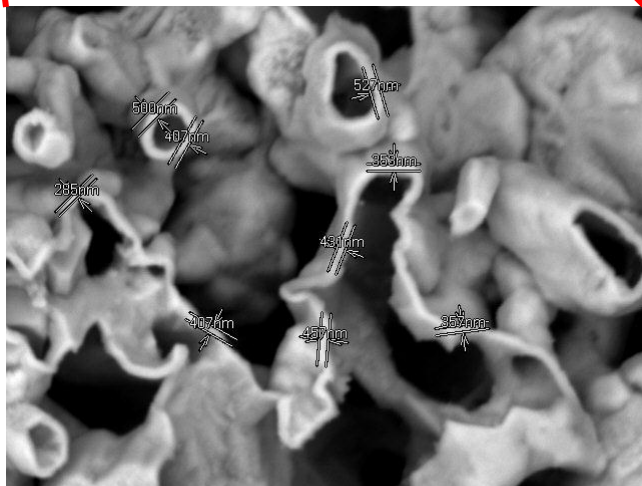
Zn-Fulleride + Zn Nanowire Composites



Zinc Phosphide Nanotube Growth

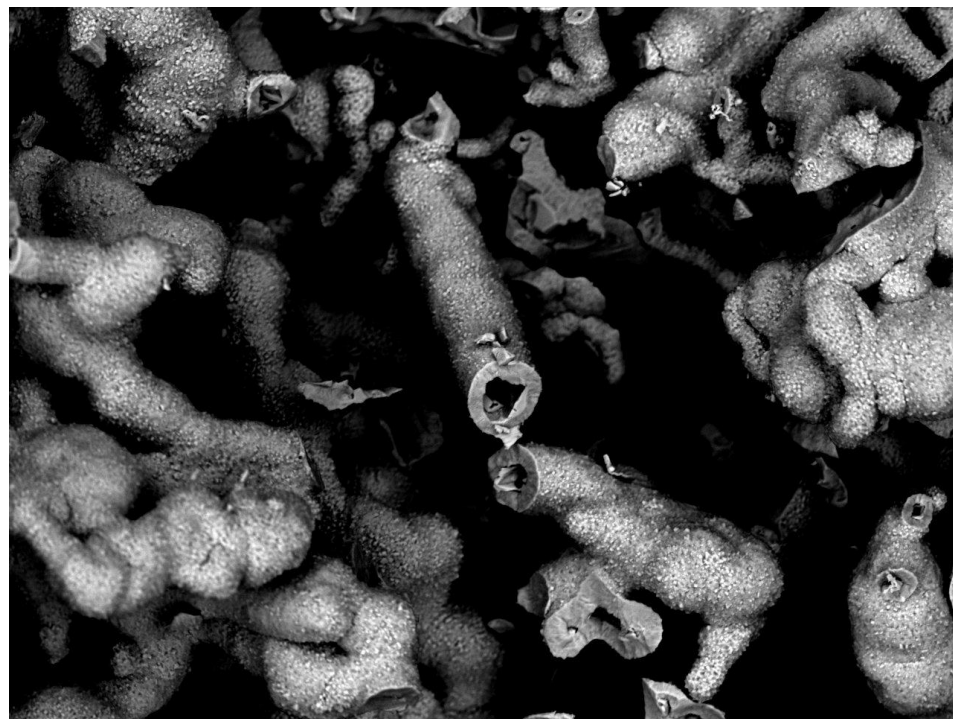


Zn₃P₂ tube 2012/01/11 10:03 H D4.6 x1.0k 100 um



Zn₃P₂ tube 2012/01/11 10:07 H D4.5 x5.0k 20 um

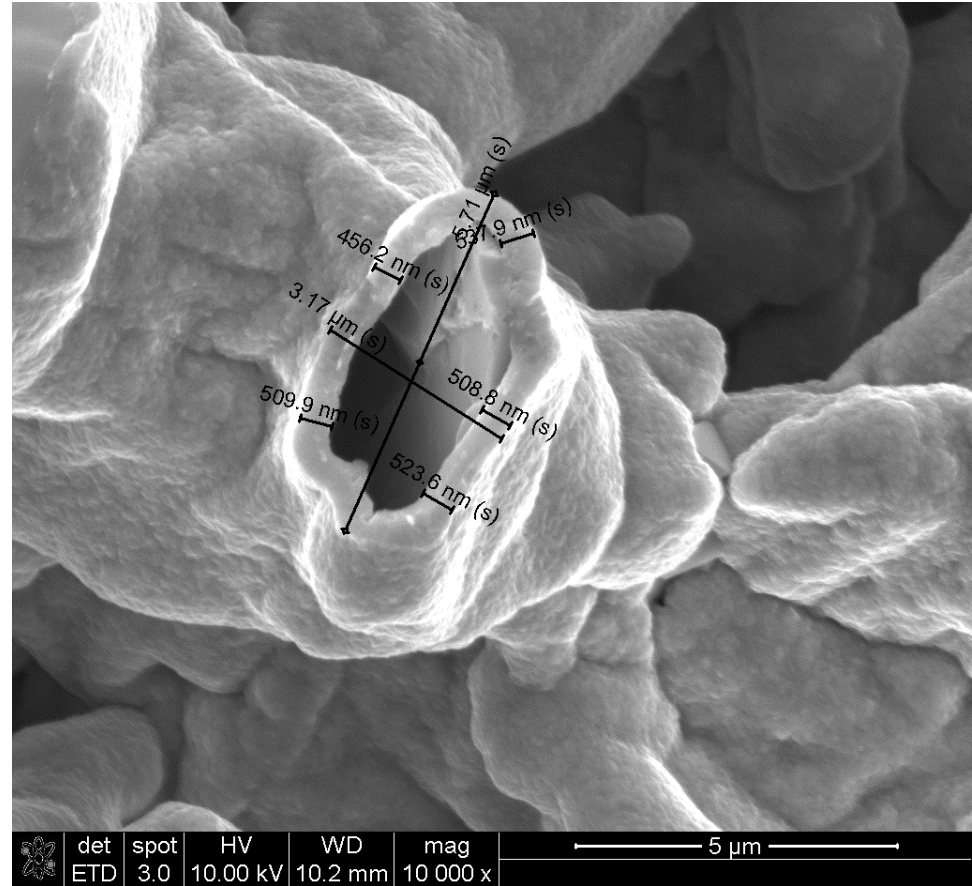
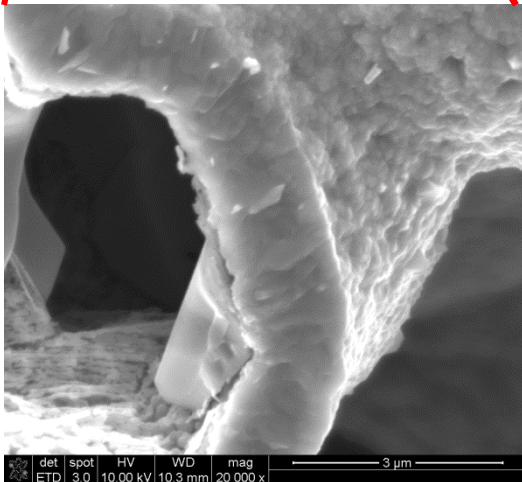
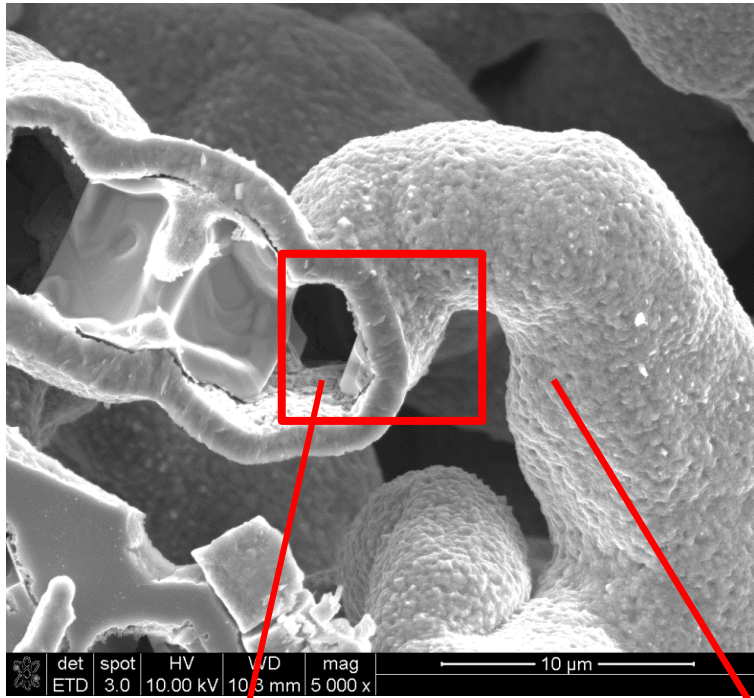
- Zinc nanowire were first grown under std conditions and then Red Phosphorus was evaporated and reacted on the tubes
- Zn₃P₂ Micro/Nanotubes were grown
- Two distinct types of tubes were identified
- Possible reaction mechanism is presented



Zn₃P₂ tube 2012/01/11 09:51 H D4.9 x800 100 um



Zinc Phosphide Tubes High Res SEM

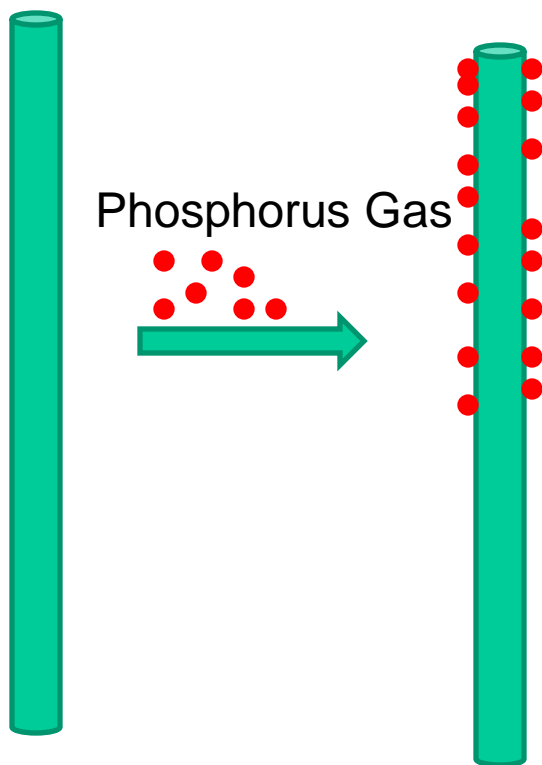




Self Templated growth of Zinc Phosphide Nanotube Growth

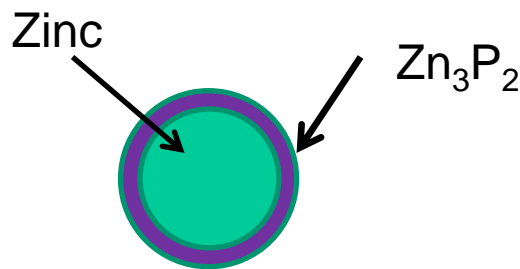
Phosphorus reaction with ZNW

Zinc Nanowire



Wire Cross Section

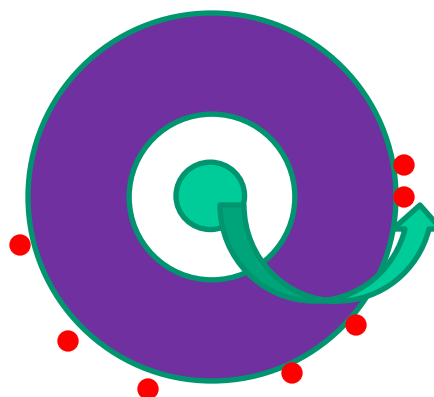
Initial creation of Zn_3P_2 monolayer



Initiation and reaction held at 400°C

Zinc Phosphide growth is mediated by template of the Zinc wires that initiate the reaction.

Zn_3P_2 Nanotube Growth



Zinc diffusing out of core



Confirmation Tests to Identify Fulleride Product



1. UV/Vis-NIR: Examine Near Infrared region of spectrum to determine oxidation state of fulleride ion. Each oxidation state has very specific $\lambda_{\text{max(es)}}$ in this region.
2. RF-ICP: Determine counter-ion/cation to fulleride
 - The ICP analysis of the THF solution containing $\text{Zn}_x(\text{C}_{60})_y$ had emission peaks at 213.86 nm from the contents of zinc and 193.09 nm from the carbon contents.
 - Leads us to believe that C_{60} is present with Zn^{2+} as its counter-ion.
3. XPS: Determine surface molecular contents of crystallized complexes of products collected
4. Raman: Determine vibrational modes present in crystallized samples.
5. EPR: Determine if fullerene is holding a charge.
6. ^{13}C -NMR: Amount of downfield shift can also determine oxidation state of fulleride, as well as determine if fulleride is present and intact
7. SEM of powder appeared to be homogenous



Conclusions



- 3 different preparation routes for fulleride synthesis
- Demonstration of ultra-low thermal conductivities
- Gradient sample were able to produce thousands of different stoichiometries on one sample

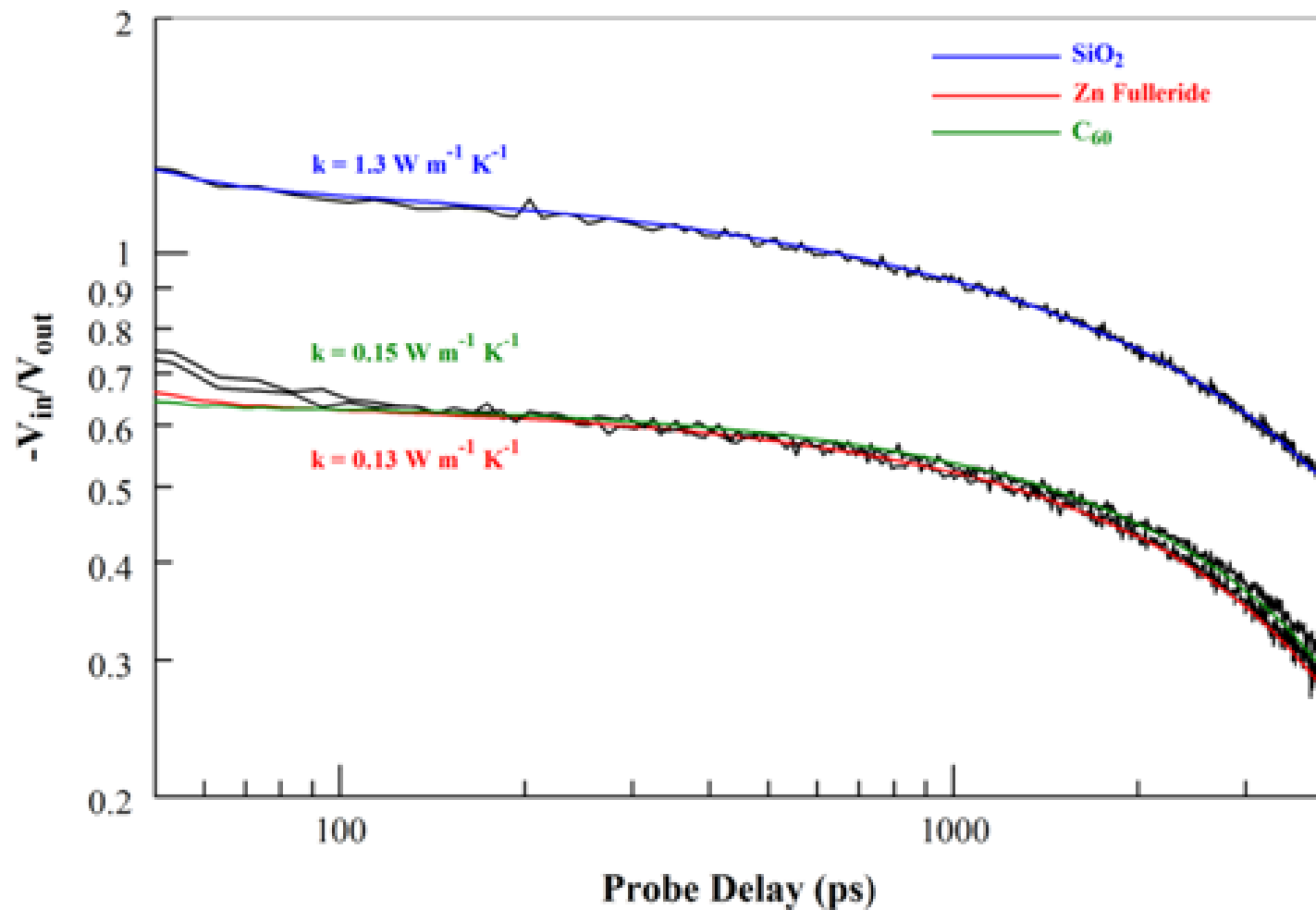


Questions?





TDTR





Third Remarkable Fullene Characteristic: Fulleride Formation



“High” T_c Molecular Superconductors

Table 6.3. Lattice constants (a_0) and position of the alkali elements for A_3C_{60} fullerides at ambient temperature

A_3C_{60}	a_0 (Å)	$A_1(T)A_2(T)A_3(O)$	Type	T_c (K)
Cs_3C_{60}	—	—	A15	40 ^a
$RbCs_2C_{60}$	14.555	$Rb(T)Cs(T)Cs(O)$	fcc	33
KCs_2C_{60}	unstable	—	fcc	—
Rb_2CsC_{60}	14.431	$Rb(T)Rb(T)Cs(O)$	fcc	31
Rb_3C_{60}	14.384	$Rb(T)Rb(T)Rb(O)$	fcc	29
KRb_2C_{60}	14.337	$K(T)Rb(T)Rb(O)$	fcc	27
K_2CsC_{60}	14.292	$K(T)K(T)Cs(O)$	fcc	24
K_2RbC_{60}	14.267	$K(T)K(T)Rb(O)$	fcc	23
K_3C_{60}	14.240	$K(T)K(T)K(O)$	fcc	19
Na_2CsC_{60}	14.126	$Na(T)Na(T)Cs(O)$	fcc \rightarrow sc	12
Na_2RbC_{60}	14.092	$Na(T)Na(T)Rb(O)$	fcc \rightarrow sc	3.5
Na_2KC_{60}	14.122	$Na(T)Na(T)K(O)$	fcc \rightarrow sc	2.5
Na_3C_{60}	14.191	$Na(T)Na(T)Na(O)$	fcc ^b	< 2 K
Li_2CsC_{60}	14.075	$Li(T)Li(T)Cs(O)$	fcc	< 50 mK
$Li_2CsC_{60}^{\#}$	14.008	$Li(T)Li(T)Cs(O)$	fcc	< 50 mK
Li_2KC_{60}	13.896	$Li(T)Li(T)Rb(O)$	—	< 50 mK
Li_2KC_{60}	multiphase	—	—	—
$Na_2Cs(NH_3)_4C_{60}$	14.473	$Na(T)Cs(T)Na(NH_3)_4(O)$	fcc	30
Ba_6C_{60}	11.182	—	bcc	6
Sr_6C_{60}	10.975	—	bcc	4
Ca_5C_{60}	14.01	—	sc	8.5
$Yb_{2.75}C_{60}$	superlattice	—	orthorhombic	6
$Sm_{2.75}C_{60}$	superlattice	—	orthorhombic	8

^a Under hydrostatic pressure.

^b Stable at $T > 180$ K.

[#] Different batch of samples.



X =

Alkali

Alkaline Earth

Transition Metal

Rare Earth Metal

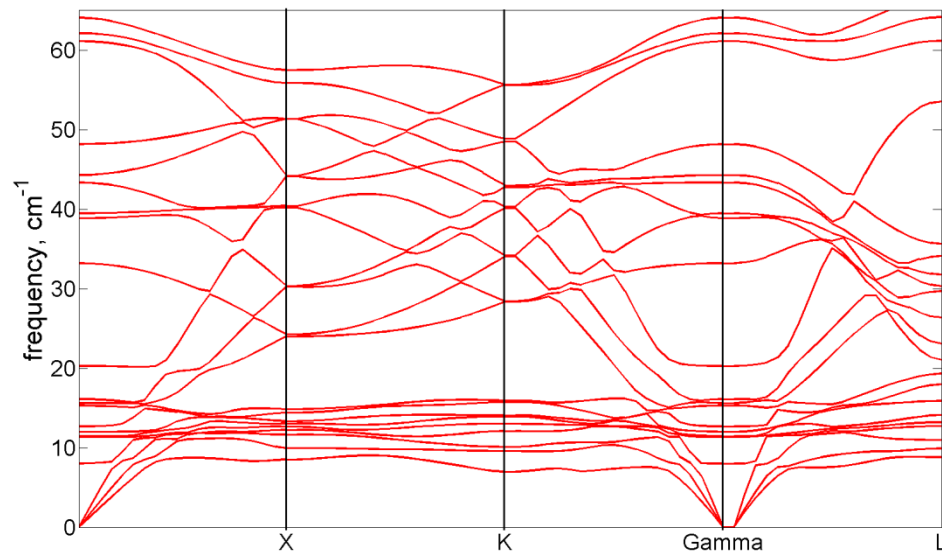
Main Group

**Many fullerides known;
semiconductive
fullerides relatively
unexplored!**

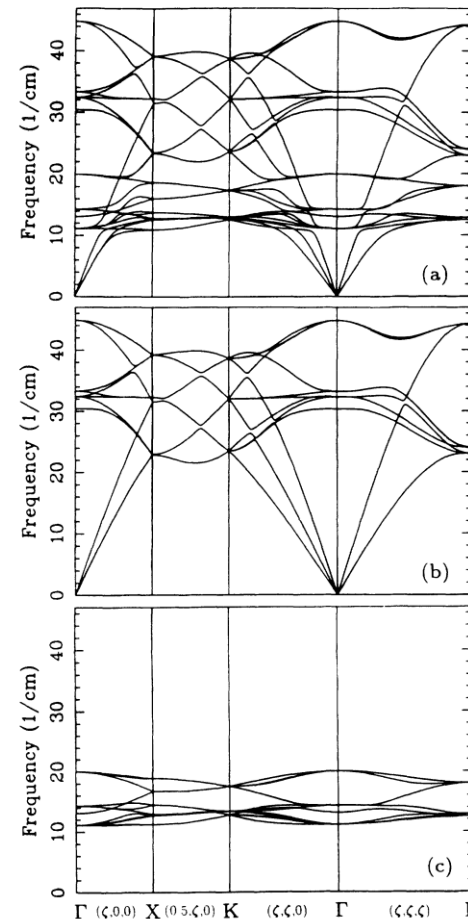
“Handbook of Conductive Molecules and Polymers,”
H. S. Nalwa, ed., Wiley & Sons, 1997, Vol. 1, p. 317



C_{60} FCC Dispersion – Validation



REBO Force Field



PHYSICAL REVIEW B

VOLUME 46, NUMBER 7

15 AUGUST 1992-I

Ground-state structural and dynamical properties of solid C_{60} from an empirical intermolecular potential

X.-P. Li

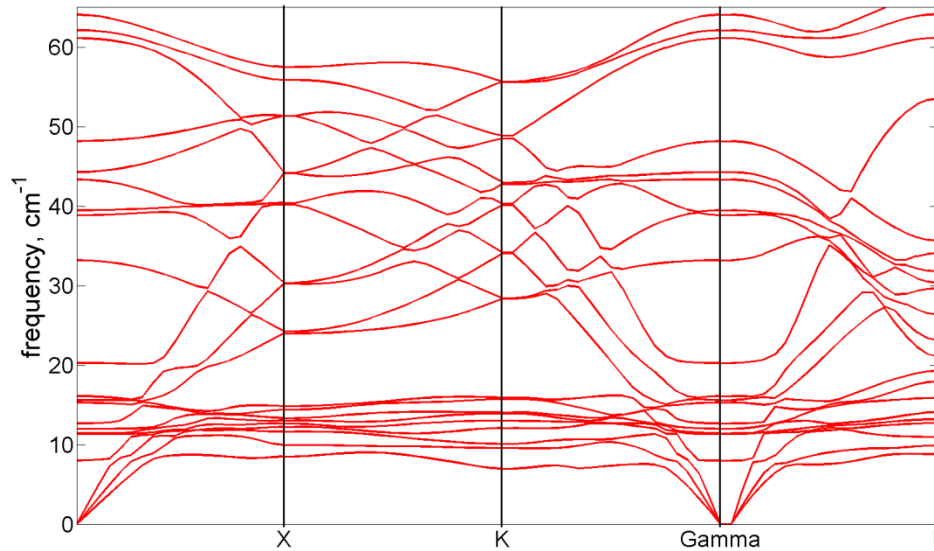
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08855

Jian Ping Lu and Richard M. Martin

*Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801
and Materials Research Laboratory, University of Illinois at Urbana-Champaign, 1110 West Green Street,
Urbana, Illinois 61801*



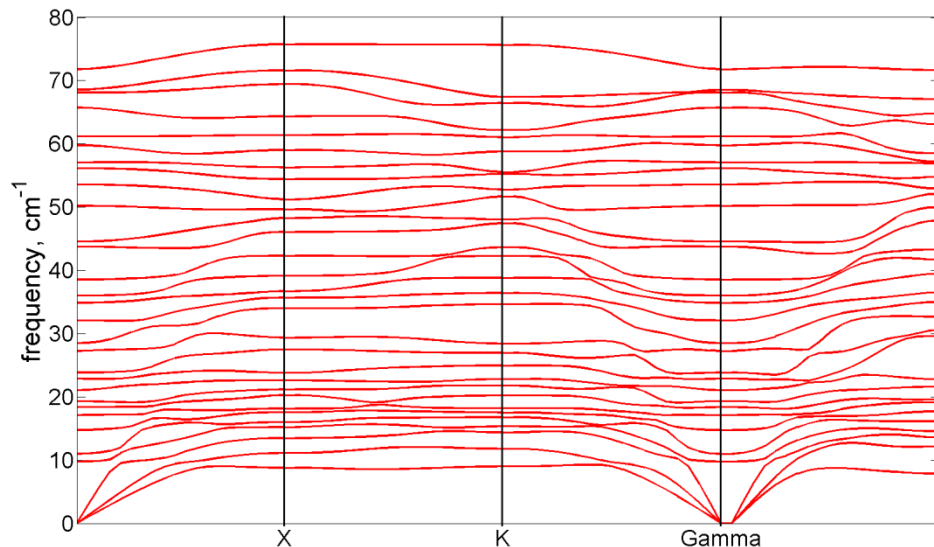
Ba₃C₆₀ BCC Dispersion and C_v



C₆₀

$$C_v = 0.026824 \text{ eV/K}$$

Molecule breaks symmetry –
lattice constants 9.98, 12.80, 12.83



Ba₃C₆₀

$$C_v = 0.015051 \text{ eV/K}$$

Still plotting the high symmetry
points of FCC. Group velocities
appear lower

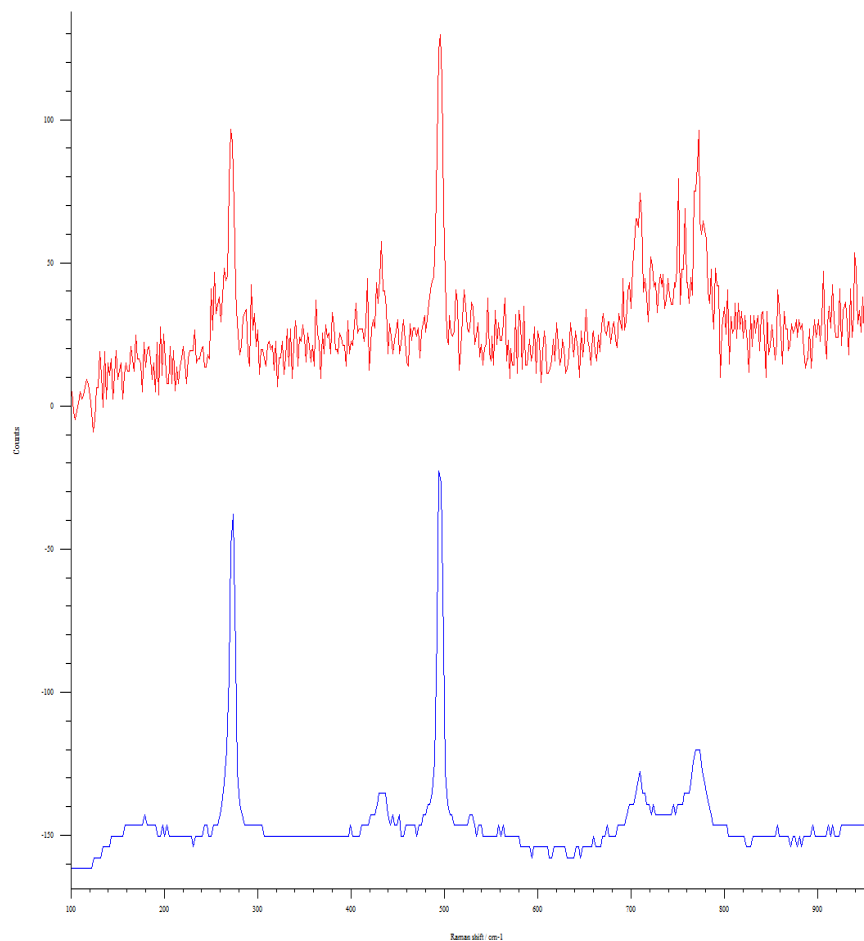
$$k = \frac{1}{3} C_v v_g l$$



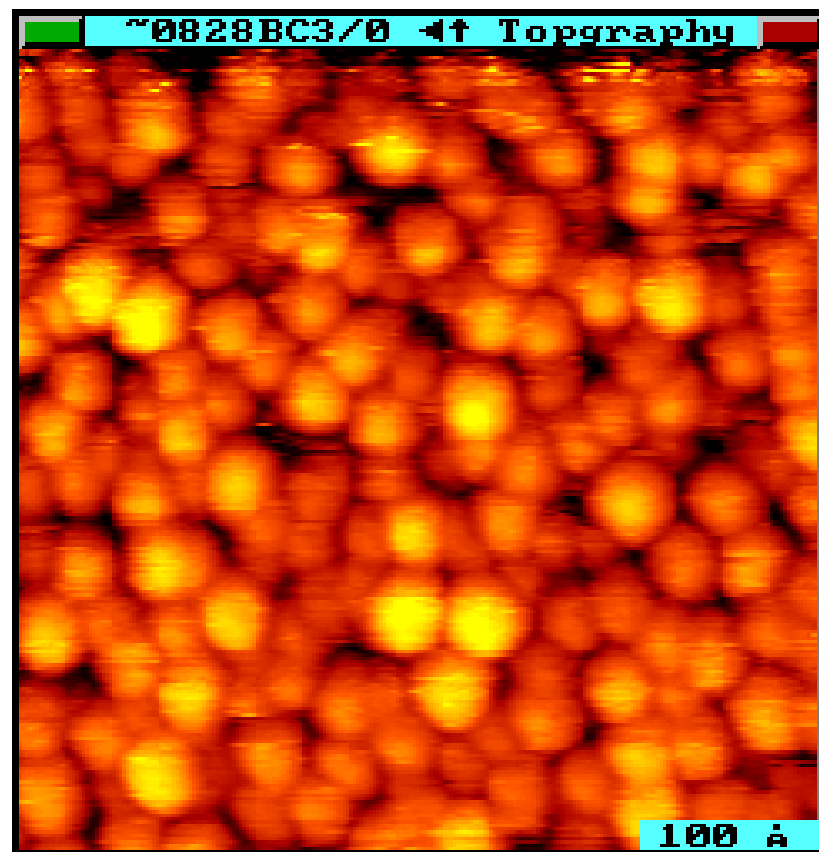
Thermal Evaporation of C₆₀



Raman Spectra of Thermal Evap C₆₀



Visible	Ht	Quality	Library	Spectrum Info	Library Index
	1	0.342296	Inorgan.lib	Buckminster Fullerene (Organic)	561
	2	0.169309	Inorgan.lib	Buckminster Fullerene (Organic)	789



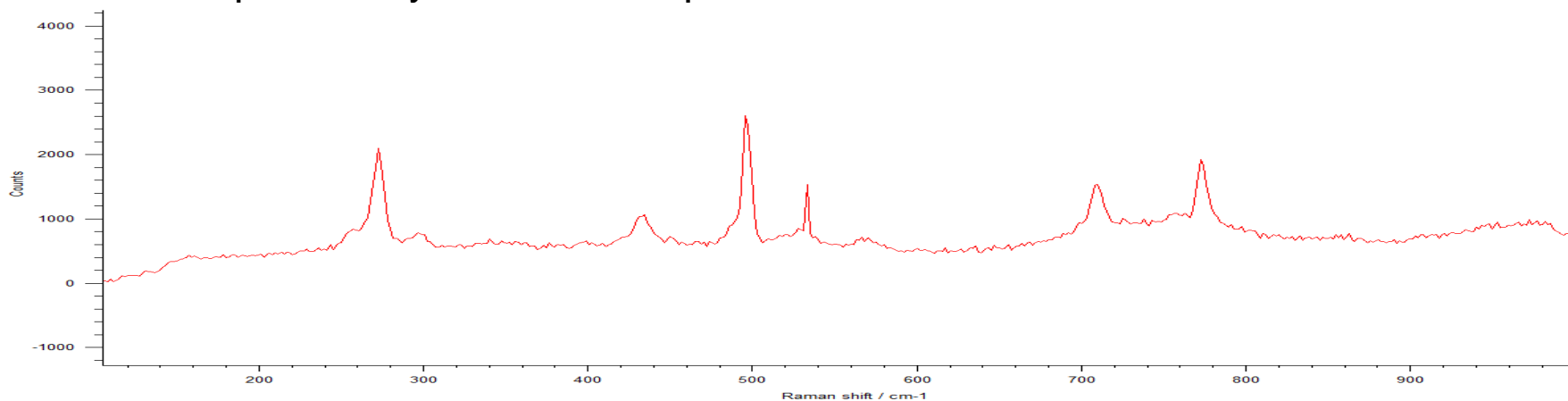
STM Image Courtesy of Dr. Altfeder



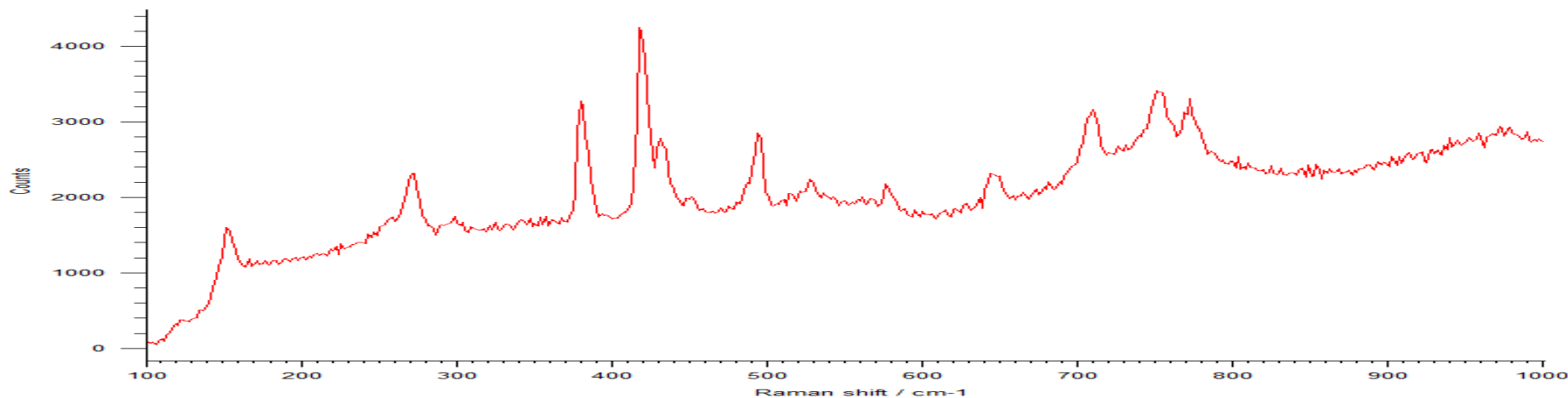
Raman Spectroscopy of C_{60}

Sample is 75 Layers of C_{60} and Zn (C_{60} and Zn Layers are 10nm thick) After Annealing in furnace at $400^{\circ}C$

Pure C_{60} – Deposited by Thermal Evap



Zn- C_{60} after the anneal

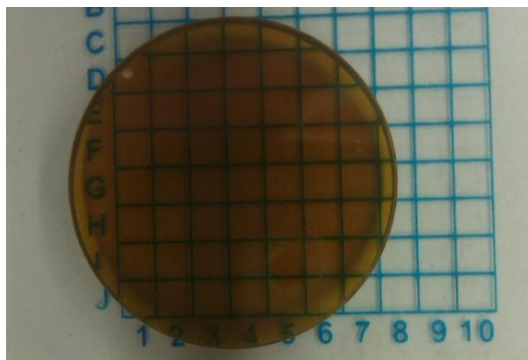
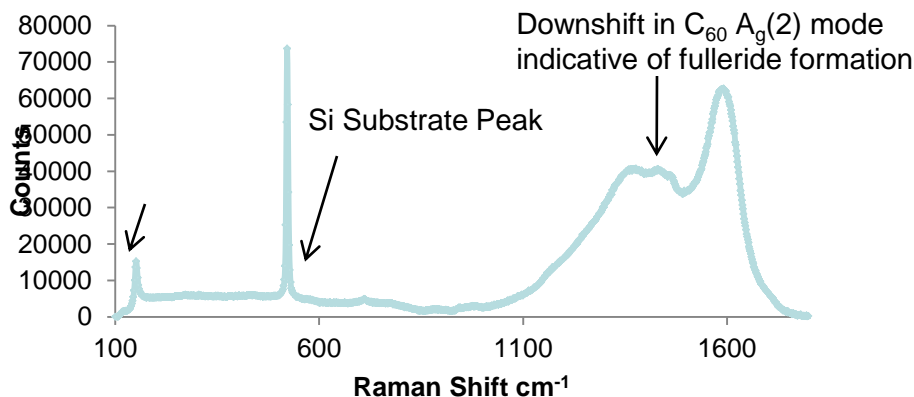




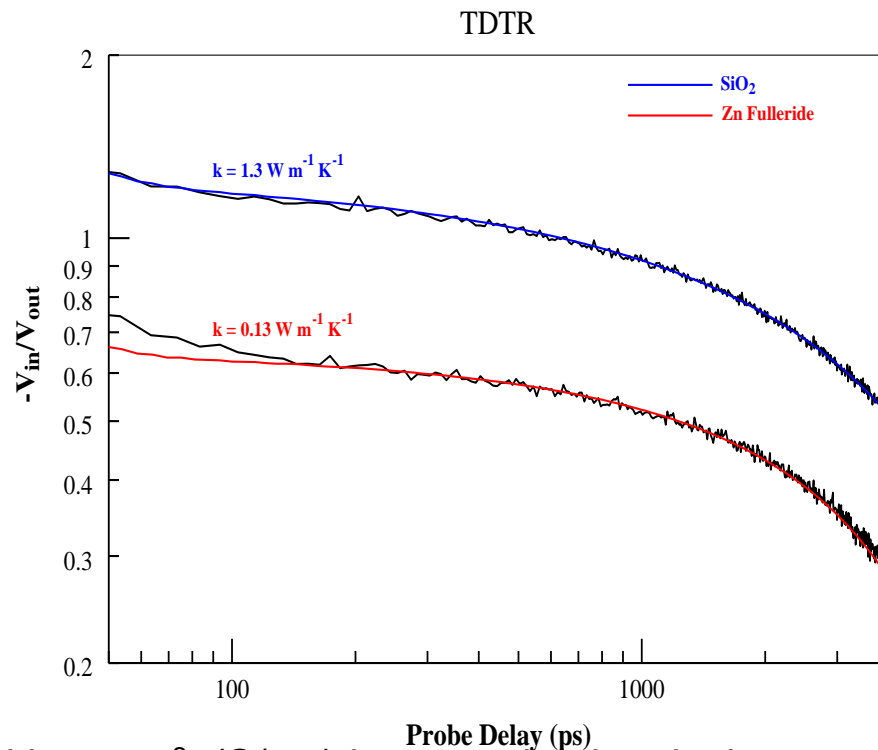
Project Results: Increased σ , Decreased κ And ...



Zn_xC_{60} after Anneal Step



Time domain thermal reflectance data of Fulleride materials shows a 10x reduction in Thermal conductivity compared to glass



SUCCESSSES:

- Exceptionally good phonon blocking achieved with a $\sim 10^8$ (S/cm) increase in electrical conductivity
- Construction of automated thermal evaporator for layered materials synthesis
- Unanticipated optically transparent electrically conductive films created